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KVB, Inc, Tustin, Calif

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Emission Reduction on Two Industrial Boilers with Major Combustion Modifications

Interagency Energy/Environment R&D Program Report

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Emission Reduction on Two Industrial Boilers with Major Combustion Modifications

by

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16. ABSTRACT The report gives results of a study of the effects on pollutant emissions of extensive combustion modifications on two industrial boilers. Staged combustion, variable excess air, and variable air preheat were evaluated while firing natural gas or No. 6 fuel oil in a watertube boiler rated at 16 MW thermal input (55 million Btu/hr). Reductions in NOx of 31% for natural gas and 42% for No. 6 fuel oil were obtained when excess air was optimized and staged air was introduced through injection ports in the furnace side, as far downstream from the burner as practical. Combined lowered air preheat and staged combustion reduced NOx by 70% while firing natural gas. In a watertube boiler rated at 6.5 MW thermal input (22 million Btu/hr), flue gas recirculation, staged combustion, and variable excess air were evaluated while firing natural gas, No. 2 fuel oil, or No. 6 fuel oil. The maximum NOx reduction for natural gas was 79% with flue gas recirculation and lowered excess air. A 77% NOx reduction was obtained for No. 2 fuel oil with combined modifications. Since NOx reduction for heavy fuel oil has been very difficult to achieve, the most significant result in the program was a 55% NOx reduction, obtained with a combination of modifications while firing No. 6 fuel oil. Trace species and organics emissions were measured while firing No. 6 fuel oil.

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Burners	Fuel Oil	Industrial Boilers		
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SECTION 1.0

SUMMARY

1.1 OBJECTIVE AND SCOPE

The objective of this program was to evaluate the effectiveness of combustion modifications and operating variable changes as means of improvement in thermal efficiency and for emissions control in industrial size watertube boilers. These techniques have previously been shown to be effective on industrial boilers (Refs. 1, 2) and the purpose of this program was to evaluate feasibility of implementing each candidate combustion modification independently and in various combinations.

The program scope provided for tests on two watertube boilers to evaluate low excess air, variable combustion air preheat, staged combustion air, and flue gas recirculation while firing natural gas, #2 and #6 oil at Location 19 and natural gas and #6 oil at Location 38. Emissions to be measured were NO, NO_x, SO_2, SO_3, CO, CO_2, O_2, gaseous hydrocarbons, particulates, particulate size distribution, smoke number and opacity.

On four tests at Location 19,samples were collected for analysis of trace species and selected organic emissions. Two of these tests were at baseline operating conditions and two were at low NO_x conditions.

This is a final report on this test program documenting the test equipment, a summary of the test data and a discussion of the data in relation to each type of combustion modification.

1.2 TEST PROCEDURES

Parametric tests were conducted to evaluate the effectiveness of combustion modifications on emissions reduction and boiler thermal efficiency. For natural gas, #2 oil and #6 oil, the effect of lowered excess air, staged combustion air, variable air preheat, flue gas recirculation and combinations of these, was evaluated.

A government-owned mobile laboratory was used for measuring air pollutant emissions and unit efficiency parameters at Location 19. The mobile laboratory contains analytical instrumentation for continuous measurement of NO, NO_x, SO_2, CO, CO_2, O_2, and gaseous hydrocarbons. Sulfur oxides (SO_2 and SO_3), total particulate, and particulate size distribution were measured and analyzed by grab sample techniques. Four tests were conducted to sample and analyze for trace species and selected organics using the source assessment sampling system (SASS train).

Gaseous emissions were measured at Location 38 using a KVB mobile laboratory containing analytical instrumentation for continuous measurement of NO, NO_x, CO, O_2, CO_2, and hydrocarbons. Sulfur oxides (SO_2 and SO_3), total particulate and particulate size distribution were measured using grab sample techniques.

1.3 RESULTS AT LOCATION 19

Results of combustion modification tests at Location 19 with natural gas, #2 oil and #6 oil are summarized in Table 1-1 where NO_x reduction as a function of combustion modification technique is tabulated. The greatest reduction with both #2 and #6 oil was obtained with a combination of all three techniques - low O_2, flue gas recirculation and staged combustion air. With natural gas, the greatest NO_x reduction was with flue gas recirculation and low O_2.

Results of particulate measurements obtained using EPA Method 5 are shown in Table 1-2. The minimum total particulate measurements were obtained at the low NO_x condition for each fuel. The same was true for solid particulate with the exception of No. 2 oil, for which minimum particulate was obtained with FGR and low O_2.

TABLE 1-1. SUMMARY OF NO_x REDUCTION AS A FUNCTION OF COMBUSTION MODIFICATION TECHNIQUES FOR VARIOUS FUELS - LOCATION 19

Fuel Type	No. 2 Oil (0.008% N)	No. 6 Oil (0.20% N)	Natural Gas
Average Baseline NO_x, ppm at 3% O_2	114	220	96* 92†
Combustion Modification Technique	NO_x Reduction, Percent of Baseline		
Lowered Excess Air	20	30	19* 3†
Staged Combustion Air (SCA), Normal O_2	30	29	32* 46†
SCA, Low O_2	44	42	42*
Flue Gas Recirculation (FGR), Normal O_2	68	11	77†
FGR, Low O_2	73	40	$\boxed{79}$†
FGR + SCA, Normal O_2	69	53	76†
FGR + SCA, Low O_2	$\boxed{77}$	$\boxed{55}$	§†

*Ring burner

†Gas gun burner

§Stability limits prevented lowering O_2

☐ Indicates lowest NO_x mode

TABLE 1-2. SUMMARY OF METHOD 5 PARTICULATE MEASUREMENTS
FOR LOCATION 19 STEAM BOILER

Boiler Operating Mode	No. 2 Oil		No. 6 Oil		Natural Gas	
	Total ng/J (lb/MMBtu)	Solid ng/J (lb/MMBtu)	Total ng/J (lb/MMBtu)	Solid ng/J (lb/MMBtu)	Total ng/J (lb/MMBtu)	Solid ng/J (lb/MMBtu)
Baseline	24.24 (0.0564)	2.595 (0.0060)	36.21 (0.084)	27.55 (0.064)	3.68 (0.0086)	1.92 (0.0045)
Low O_2	16.29 (0.0379)	5.95 (0.0138)	28.87 (0.0672)	25.80 (0.060)		
SCA	11.6 (0.0270)	9.01 (0.0210)	31.8 (0.0743)	27.2 (0.0635)		
FGR, Low O_2	5.84 (0.0136)	1.95 (0.0045)	32.33 (0.075)	29.36 (0.068)	2.63 (0.0061)	1.67 (0.0039)
FGR + SCA	4.16 (0.0097)	3.31 (0.0077)	28.80 (0.0670)	9.10 (0.021)		

☐ indicates lowest NO_x mode

Boiler thermal efficiency was calculated using the ASME heat loss method. The results of these measurements are shown in Table 1-3. The change in boiler efficiency at the low NO_x conditions is shown for each fuel.

Four trace species and organics tests were conducted at Location 19 with the boiler firing No. 6 oil. The first two tests were with the boiler in the normal or baseline conditions and the next two tests were with the boiler in the low NO_x operating mode. Samples for the first baseline test were not analyzed because of a major change in fuel supply. The results of these tests are summarized in Table 1-4. Additional data on the specific POM compounds present in the SASS Train XAD-2 adsorbant are shown in Table 1-5.

1.4 RESULTS AT LOCATION 38

A summary of NO_x reduction as a function of modification technique is presented in Table 1-6 for the tests conducted at Location 38. NO_x reductions of 43% and 32% with No. 6 oil and natural gas, respectively, were achieved using a combination of staged combustion air and lowered excess oxygen. Combined staged combustion and lowered air preheat produced 69% reduction of NO_x, compared to baseline NO_x emissions.

Results of the particulate measurements obtained using EPA Method 5 are presented in Table 1-7 for No. 6 fuel oil. For all modifications the total particulate emissions were reduced by up to 34% compared to baseline emissions. Solid particulates were increased slightly (up to 8%) with all modifications, compared to baseline emissions.

TABLE 1-3. SUMMARY OF CHANGE IN BOILER EFFICIENCY DUE TO COMBUSTION MODIFICATIONS AT LOCATION 19

Boiler Operating Mode	No. 2 Oil	No. 6 Oil	Natural Gas
Low O_2	+ 1.5%	+ 1.5%	- 1.2%* + 0.9%†
SCA, Normal O_2	+ 0.9%	+ 0.1%	+ 0.1%* + 0.3%†
SCA, Low O_2	+ 1.1%	+ 0.8%	+ 0.5%*
FGR, Normal O_2	- 1.9%	- 0.7%	- 0.8%†
FGR, Low O_2	+ 0.9%	+ 0.6%	$\boxed{-\ 0.6\%^{\dagger}}$
FGR + SCA, Normal O_2	- 1.2%	- 0.8%	- 0.5%†
FGR + SCA, Low O_2	$\boxed{-\ 0.8\%}$	$\boxed{+\ 0.1\%}$	§

*Ring burner

†Gas gun burner

§Stability limits prevented lowering O_2

☐ Indicates lowest NO_x mode

TABLE 1-4. SUMMARY OF TOTAL TRACE SPECIES AND ORGANICS EMISSIONS FOR THE MODIFIED BOILER AT LOCATION 19 FIRING #6 FUEL OIL

	Total Emission Concentrations by Atomic Absorption, $\mu g/m^3$			Total Emission Concentrations by Spark Source Mass Spectrometry, $\mu g/m^3$		Best Mass Balances Using Either AA or SSMS Data		
Test	19-2	19-3	19-4	19-2	19-3	19-2	19-3	19-4
Condition	Baseline	Low NO_x	Low NO_x	Baseline	Low NO_x	Baseline	Low NO_x	Low NO_x
Antimony	< 380	< 540	< 350	11	160	--	--	< DL
Arsenic	6.5 < 15	59 < 64	55	6.5	6 < 12	0.26	1.7	1.60
Barium	95 < 210	640 < 740	800 < 850	MC	640	2.30	1.90	2.30
Beryllium	< 6	< 8.9	< 6	0.055 < 3	0.3 < 2	--	--	< DL
Cadmium	13	4.8 < 12	1.1 < 6	7.5 < 13	0.09 < 5	> 1.05	--	> 0.05
Calcium	650	2000	440 < 460	2080 < MC	67 < MC	0.80	0.55	0.12
Chromium	750	740	530	960	500	23.00	2.90	3.00
Cobalt	65 < 130	79 < 150	18 < 85	8 < MC	94	0.31	0.54	0.10
Copper	32	39 < 44	95	49	130	0.30	1.00	0.74
Iron	4300	4700	3100	1300 < MC	1100	1.35	0.89	2.50
Lead	45 < 70	9.9 < 21	< 15	52 < 67	54	0.83	--	< DL
Manganese	70	99	65	69	64	0.61	1.66	1.62
Mercury	< 1.9	0.06 < 21	2	NR	NR	--	--	--
Nickel	1300 < 1400	1600	2200	180 < MC	240 < MC	1.20	0.83	1.10
Selenium	< 12	9.9 < 290	< 11	2 < 5	100 < 110	--	1.40	< 0.15
Tellurium	< 300	< 450	< 290	0.04 < 3	0.2 < 3	--	--	< DL
Tin	< 750	< 1000	< 700	0.4 < 8	12	--	--	< DL
Titanium	70 < 1600	120 < 2500	20 < 100	53	580	0.92	1.40	> 0.22
Vanadium	3200 < 3400	3400 < 3600	2400	8 < MC	9 < MC	1.00	0.80	0.18
Zinc	370	810	3300	MC	680	1.30	1.60	15.00
Chloride	12000	3500	6000	4.3	2100	--	17.00	46.00
Fluoride	170 < 180	64 < 79	24 < 33	23	170	0.52	0.70	0.09
Nitrates	130	110 < 120	85	--	--	--	--	--
Sulfates	18000	18000	21000	--	--	--	--	--
Total POM	NES	50 < 51	NES	--	--	--	--	--
Total PCB	NES	< 7	NES	--	--	--	--	--

See notes on Table 3-8, page 62

TABLE 1-5. POM COMPOUNDS IN THE XAD-2 RESIN DETERMINED BY GAS CHROMATOGRAPH-MASS SPECTROMETRY, LOCATION 19

POM Component	Test 19-2, Baseline		Test 19-3, Low NO_x	
	ng/g	ng/m^3	ng/g	ng/m^3
Anthracene	3.2	24	0.45	3.4
Phenanthrene	--	--	0.02	0.1
*Methyl Anthracenes	0.2	1.6	0.12	0.9
Fluoranthene	1.2	9.0	0.13	0.9
Pyrene	0.05	0.4	0.05	0.4
*Benzo(c)phenanthren	0.002	0.02	--	--
Chrysene	0.03	0.19	0.004	0.03
Benzo Fluoranthenes	0.007	0.05	0.007	0.05
*Benz(a)pyrene	0.004	0.032	--	--
Benz(e)pyrene	0.004	0.032	--	--
Total POM	4.74	35.5	0.78	5.8

*Compounds required to be identified

Note: Values in this table are expressed in nanograms (ng), (1 ng = 10^{-9} g). Values in other trace species and organics tables in this report are expressed in micrograms (μg), (1 μg = 10^{-6} g).

TABLE 1-6. SUMMARY OF NOx REDUCTION AS A FUNCTION OF COMBUSTION MODIFICATION TECHNIQUE FOR NUMBER 6 FUEL OIL AND NATURAL GAS

Location 38

Modified Condition	No. 6 Oil	Natural Gas
Lowered excess air	20%	14%
Staged combustion air (normal O_2)	36%	23%
Staged combustion air (low O_2)	$\boxed{43\%}$	32%
Variable preheat (max. temp.)	-4%	-24%
Variable preheat (min. temp.)	18%	24%
Staged combustion air & variable preheat	--	$\boxed{69\%}$

☐ Indicates lowest NO_x mode

TABLE 1-7. SUMMARY OF METHOD 5 PARTICULATE MEASUREMENTS FOR LOCATION 38 STEAM BOILER WITH #6 FUEL OIL

Condition	Total Particulate ng/J (lb/MMBtu)	Solid Particulate ng/J (lb/MMBtu)
Baseline	66.4 (0.154)	36.6 (0.085)
Low Excess Air	47.6 (0.110)	38.3 (0.088)
	43.7 (0.101)	38.7 (0.089)
Staged Combustion Air	52.6 (0.122)	38.7 (0.090)
	62.2 (0.144)	39.9 (0.092)
Variable Air Preheat (Minimum Temperature)	54.4 (0.126)	37.6 (0.087)

SECTION 2.0

INSTRUMENTATION AND TEST PROCEDURES

2.1 LOCATION 19 INSTRUMENTATION

The emissions measurements were made using analytical instruments and equipment contained in a government-furnished mobile instrumentation laboratory contained in an 2.4 x 9.1 meter (8 x 30 ft) trailer. A plan and side view of the trailer are shown in Figure 2-1. Gaseous emission measurements are made with the following analytical instruments:

Emission Species	Manufacturer	Measurement Method	Model No.
Hydrocarbon	Beckman Instruments	Flame Ionization	402
Carbon Monoxide	Beckman Instruments	IR Spectrometer	865
Oxygen	Teledyne	Polarographic	326A
Carbon Dioxide	Beckman Instruments	IR Spectrometer	864
Nitrogen Oxides	Thermo Electron	Chemiluminescent	10A
Sulfur Dioxide	Dupont Instruments	UV Photometric	400

Total oxides of sulfur were measured by wet chemistry methods using the sampling train and analytical procedure of the Shell-Emeryville method. Total particulate measurements were made using an EPA Method 5 sampling train manufactured by Western Precipitation Div. of Joy Manufacturing Co. Particulate size distribution was measured using an Andersen 2000 cascade impactor. Smoke density was measured using an automated Bacharach smoke spot pump. Samples for trace species and organics analysis were taken with the source assessment sampling system (SASS train), a high volume sampling train.

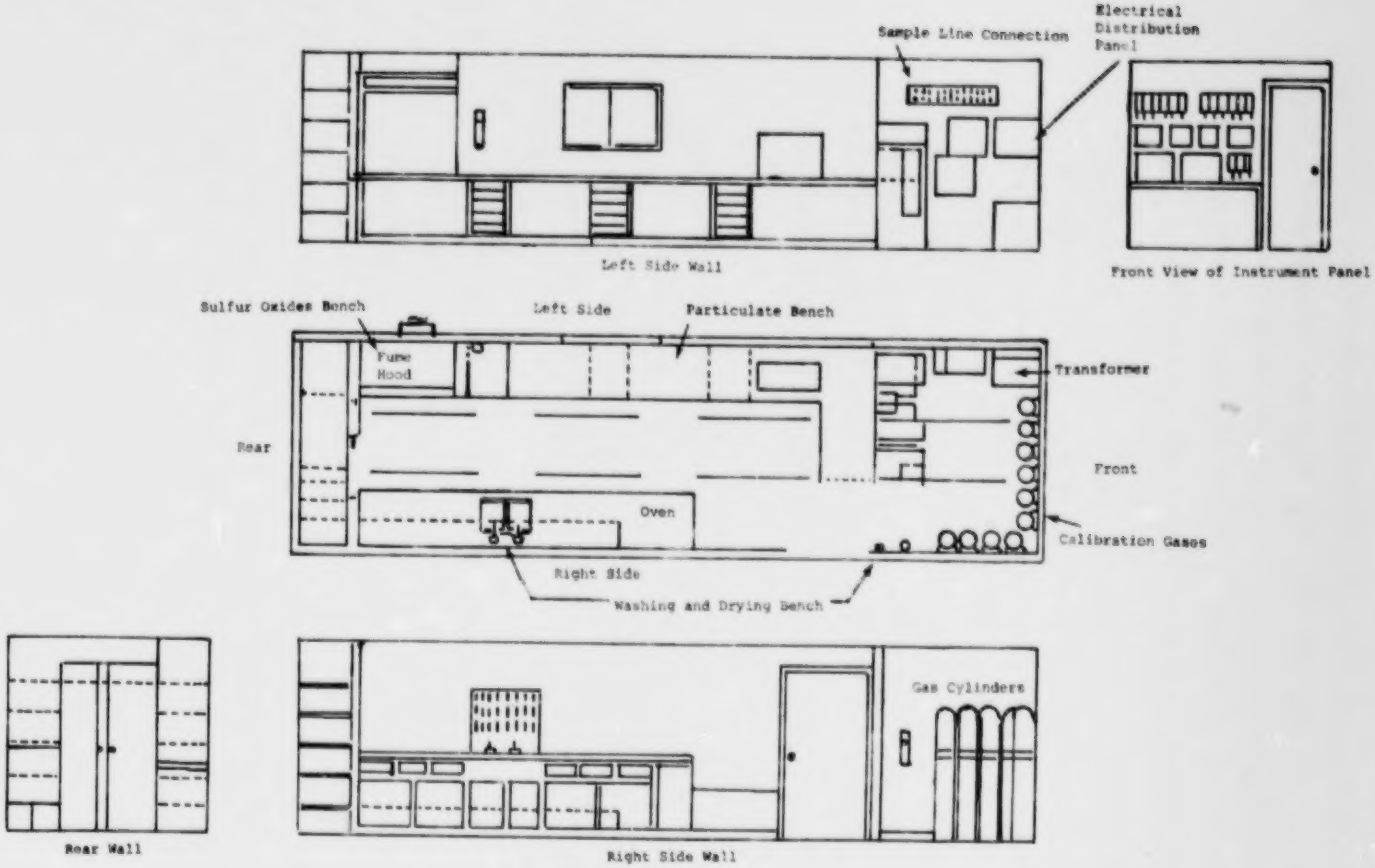


Figure 2-1. Instrumentation trailer floor plan and side wall elevation.

2.1.1 Gaseous Emissions

The laboratory is equipped with analytical instruments to continuously measure concentrations of NO, NO_x, CO, CO_2, O_2, SO_2, and hydrocarbons. The sample gas is delivered to the analyzers at the proper condition and flow rate through the sampling and conditioning system described in the previous sections. This section describes the analytical instrumentation.

Total Nitrogen Oxides

The oxides of nitrogen monitoring instrument used is a Thermo Electron chemiluminescent nitric oxide analyzer. The operational basis of the instrument is the chemiluminescent reaction of NO and O_3 to form NO_2 in an excited state. Light emission results when excited NO_2 molecules revert to their ground state. The resulting chemiluminescence is monitored through an optical filter by a high sensitivity photomultiplier tube, the output of which is electronically processed so it is linearly proportional to the NO concentration.

Air for the ozonator is drawn from ambient through an air dryer and a 10-micron filter element. Flow control for the instrument is accomplished by means of a small bellows pump mounted on the vent of the instrument downstream of a separator which insures that no water collects in the pump.

The basic analyzer is sensitive only to NO molecules. To measure NO_x (i.e., NO + NO_2), the NO_2 is first converted to NO. This is accomplished by a converter which is included with the analyzer. The conversion occurs as the gas passes through a thermally insulated, resistance heated, stainless steel coil. With the application of heat, NO_2 molecules in the sample gas are reduced to NO molecules, and the analyzer then reads NO_x. NO_2 is obtained by the difference in readings obtained with and without the converter in operation.

Specifications

Accuracy: 1% of full scale

Span stability: ± 1% of full scale in 24 hours

Zero stability: ± 1 ppm in 24 hours

Power requirements: 115 ± 10V, 60 Hz, 1000 watts

Response: 90% of F.S. in 1 sec (NO_x mode); 0.7 sec (NO mode)

Output: 4-20 ma

Sensitivity: 0.5 ppm

Linearity: ± 1% of full scale

Vacuum detector operation

Range: 2.5, 10, 25, 100, 250, 1000, 2500, 10,000 ppm F.S.

Both the total nitrogen oxides (NO_x) and nitric oxide (NO) concentrations are measured directly using a sample line heated to about 394 K (250 °F) to conduct the gas sample to the analyzer in the trailer. In addition, the nitric oxide concentration is measured sequentially using an unheated sample line connected to the same analyzer in the trailer. Here, the water is first removed from the sample gas by a drop-out bottle and a refrigerator.

Carbon Monoxide and Carbon Dioxide

Carbon monoxide and carbon dioxide concentrations are measured by Beckman Model 864 and 865 short pathlength nondispersive infrared analyzers. These instruments measure the differential in infrared energy absorbed from energy beams passed through a reference cell (containing a gas selected to have minimal absorption of infrared energy in the wavelength absorbed by the gas component of interest) and a sample cell through which the sample gas flows continuously. The differential absorption appears as a reading on a scale of 0 to 100% and is then related to the concentration of the specie of interest by calibration curves supplied with the instrument. A linearizer is supplied with each analyzer to provide a linear output over the range of interest. The operating ranges for the CO analyzer are 0-100 and 0-2000 ppm, while the ranges for the CO_2 analyzer are 0-5% and 0-20%.

Specifications

Span stability: ± 1% of full scale in 24 hours

Zero stability: ± 1 ppm in 24 hours

Ambient temperature range: 273 to 322 K (32 °F to 120 °F)

Line voltage: 115 ± 15V rms

Response: 90% of F.S. in 0.5 or 2.5 sec

Linearity: Linearizer board installed for one range

Precision: ± 1% of full scale

Output: 4-20 ma

Oxygen

A Teledyne Model 326A oxygen analyzer is used to automatically and continuously determine the oxygen content of the flue gas sample. Oxygen in the flue gas diffuses through a Teflon membrane and is reduced on the surface of the cathode. A corresponding oxidation occurs at the anode internally and an electric current is produced that is proportional to the concentration of oxygen. This current is measured and conditioned by the instrument's electronic circuitry to give a final output in percent O_2 by volume for operating ranges of 0% to 5%, 0% to 10%, and 0% to 25%.

Specifications

Precision: ± 1% of full scale

Response: 90% in less than 40 sec

Sensitivity: 1% of low range

Linearity: ± 1% of full scale

Ambient temperature range: 273 K to 325 K (32 to 125 °F)

Fuel cell life expectancy: 40,000+ hrs

Power requirement: 115 VAC, 50-60 Hz, 100 watts

Output: 4-20 ma

Total Hydrocarbons

Hydrocarbons are measured using a Beckman Model 402 hydrocarbon analyzer which utilizes the flame ionization method of detection. The sample is filtered and supplied to the burner by means of a pump and flow control system. The sensor, which is the burner, has its flame sustained by regulated flows of hydrogen fuel and air. In the flame, the hydrocarbon components of the sample undergo a complete ionization that produces electrons and positive ions. Polarized electrodes collect these ions, causing a small current to flow through an electronic measuring circuit. This ionization current is proportional to the concentration of hydrocarbon atoms which enter the burner. The instrument is available with range selection from 6 ppm to 10% full scale as CH_4.

Specifications

Full scale sensitivity: adjustable from 5 ppm CH_4 to 10% CH_4

Ranges: Range multiplier switch has 8 positions: X1, X5, X10, X50, X100, X500, X1000, and X5000. In addition, span control provides continuously variable adjustment within a dynamic range of 10:1

Response time: 90% full scale in 0.5 sec

Precision: ± 1% of full scale

Electronic stability: ± 1% of full scale per 24 hours with ambient temperature change of less than 10 °F

Reproducibility: ± 1% of full scale for successive identical samples

Analysis temperature: ambient

Ambient temperature: 273 K to 317 K (32 °F to 110 °F)

Output: 4-20 ma

Air requirements: 250 to 400 cc/min of clean, hydrocarbon-free air, supplied at 2.07×10^5 to 1.38×10^6 n/m^2 (30 to 200 psig)

Fuel gas requirements: 75 to 80 cc/min of fuel consisting of 100% hydrogen supplied at 2.07×10^5 to 1.38×10^6 n/m^2 (30 to 200 psig)

Electric power requirements: 120 V, 60 Hz

Automatic flame indication and fuel shut-off valve

Sulfur Dioxide

A Dupont Model 400 photometric analyzer is used for measuring SO_2. This analyzer measures the difference in absorption of two distinct wavelengths (ultraviolet) by the sample. The radiation from a selected light source passes through the sample and then into the photometer unit where the radiation is split by a semi-transparent mirror into two beams. One beam is directed to a phototube through a filter which removes all wavelengths except the "measuring" wavelength, which is strongly absorbed by the constituent in the sample. A second beam falls on a reference phototube, after passing through an optical filter which transmits only the "reference" wavelength. The latter is absorbed only weakly, or not at all, by the constituent in the sample cell. The phototubes translate these intensities to proportional electric currents in the amplifier. In the amplifier, full correction is made for the logarithmic relationships between the ratio of the intensities and concentration or thickness (in accordance with Beer's Law). The output is therefore linearly proportional, at all times, to the concentration and thickness of the sample. The instrument has full scale ranges of 0-500 and 0-5000 ppm.

Specifications:

Noise: Less than 1/4%

Drift: Less than 1% full scale in 24 hours

Accuracy: (± 1% of analyzer reading)+(± 1/4% of full scale range)

Sample cell: 304 stainless steel, quartz windows

Flow rate: 6 CFH

Light source: Either mercury vapor, tungsten, or "Osram" discharge type lamps

Power rating: 500 watts maximum, 115 V, 60 Hz

Reproducibility: 1/4% of scale

Electronic response: 90% in 1 sec

Sample temperature: 378 K (220 °F)

Output: 4-20 ma d.c.

Sulfur Oxides

Measurement of SO_3 concentrations is done by wet chemical analysis using the "Shell-Emeryville" method. In this technique the gas sample is drawn from the stack through a glass probe (Figure 2-2), containing a quartz wool filter to remove particulate matter, into a system of three sintered glass plate absorbers (Figure 2-3). The first two absorbers contain aqueous isopropyl alcohol and remove the sulfur trioxide; the third contains aqueous hydrogen peroxide solution which absorbs the sulfur dioxide. Some of the sulfur trioxide is removed by the first absorber, while the remainder, which passes through as a sulfuric acid mist, is completely removed by the secondary absorber mounted above the first. After the gas sample has passed through the absorbers, the gas train is purged with nitrogen to transfer sulfur dioxide, which has dissolved in the first two absorbers, to the third absorber to complete the separation of the two components. The isopropyl alcohol is used to inhibit the oxidation of sulfur dioxide to sulfur trioxide before it gets to the third absorber.

The isopropyl alcohol absorber solutions are combined and the sulfate, resulting from the sulfur trioxide absorption, is titrated with standard lead perchlorate solution, using Sulfonazo III indicator. In a similar manner, the hydrogen peroxide solution is titrated for the sulfate resulting from the sulfur dioxide absorption.

The gas sample is drawn from the flue by a single probe made of 5 mm ID Vycor glass inserted into the duct approximately one-third to one-half way. The inlet end of the probe has a section 50 mm long by 15 mm OD which holds a quartz wool filter to remove particulate matter. It is important that the entire probe temperature be kept above the dew point of sulfuric acid during sampling (minimum temperature of 533 K). This is accomplished by wrapping the probe with a heating tape.

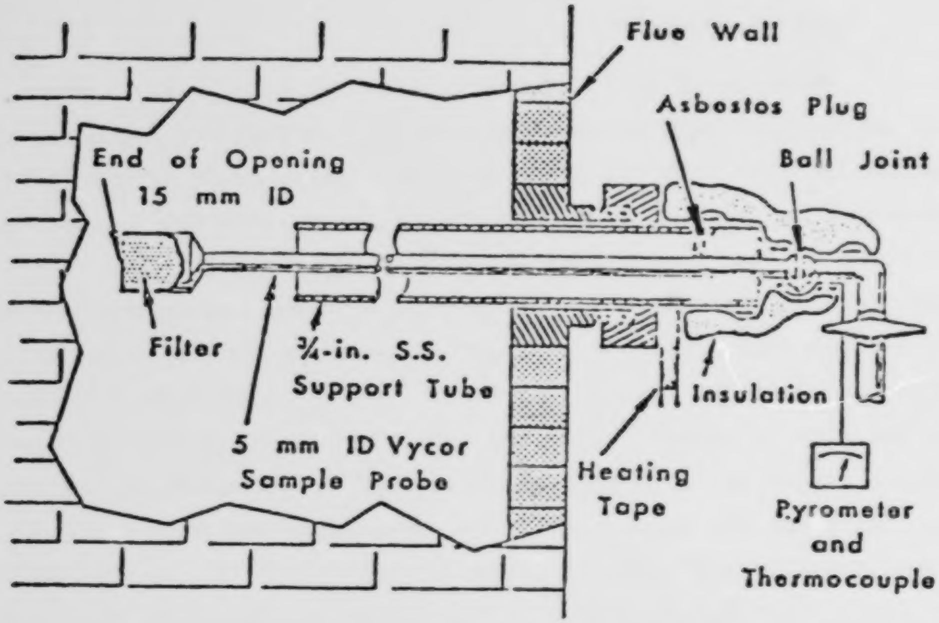


Figure 2-2. Sulfur oxides analyzer sampling probe configuration.

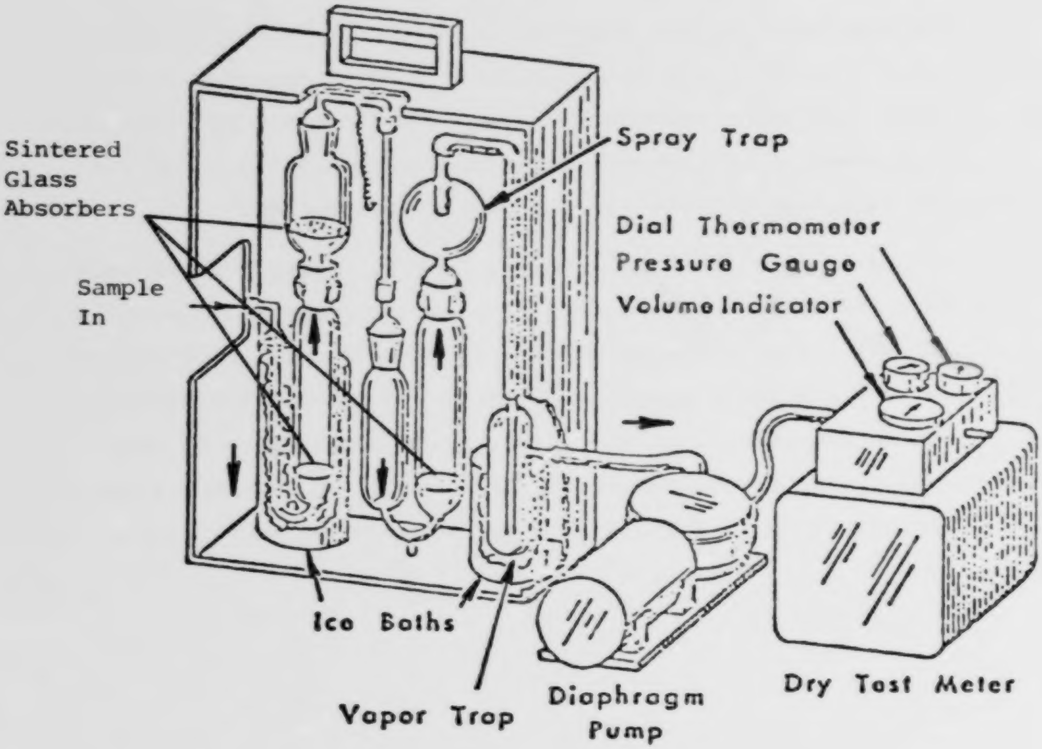


Figure 2-3. Sulfur oxides sample collection apparatus.

2.1.2 Particulate Emissions

Particulate samples are taken at the same sample port as the gas sample using a Joy Manufacturing Company portable effluent sampler. This system, which meets the EPA design specifications for Test Method 5, (Determination of Particulate Emissions from Stationary Sources, Federal Register, Volume 36, No. 27, page 24888, December 23, 1971) is used to perform both the initial velocity traverse and the particulate sample collection. Dry particulates are collected in a heated case that contains, first, a cyclone to separate particles larger than 5 microns and, second, a 100 mm glass-fiber filter for retention of particles down to 0.3 microns. Condensible particulates are collected in a train of 4 Greenburg-Smith impingers in a chilled water bath.

2.1.3 Trace Species and Organic Emissions

Particulate and gaseous samples for analysis of trace species and organics emissions at Location 19 were taken at the same stack port as the gas and standard particulate samples. The sampling system is based on a modified high volume sampling system developed by EPA and is called the "Source Assessment Sampling System" (SASS train). Dry particulates are collected in a heated case that contains three cyclones to separate particles larger than 10 µm, 3-10 µm, and 1-3 µm. Particles less than 1 µm are collected on a 142 mm glass-fiber filter. Filtered sample gas is then cooled to 293 K to 333 K (68 to 130 °F) and passed through an organic adsorbent consisting of XAD-2 chromosorb type adsorbent. Condensate is collected in a trap and the dried gas passes through an impinger train in a chilled water bath. The first impinger contains a hydrogen peroxide solution for SO_2 scrubbing and the second and third impingers contain reagents for volatile trace species collection. The fourth impinger contains Drierite for final drying prior to flow control and volume measurement equipment.

The SASS samples at a rate of 0.0019 m^3/s (4 ft^3/m). The specific train used in this program was designed to sample at 0.0019 m^3/s based on cyclone inlet conditions at 478 K (400 °F). For later trains the design was shifted to a sampling rate of 0.0019 m^3/s based on standard dry conditions. The rate of sampling has an influence on cyclone size cuts.

During sampling with the SASS, fuel samples were obtained for analysis so that emissions measured in the stack could be compared with species entering the boiler in the fuel. All sampling collections on the Location 19 boiler were while firing #6 fuel oil.

Operation of the SASS, sample recovery and handling procedures were performed in accordance with an EPA document defining sample collection procedures (Ref. 3).

Samples from the SASS train and fuel samples were analyzed by atomic absorption, spark source mass spectrometry and gas chromatography to establish the emission rates and mass balances for the species listed in Table 2-1.

2.2 LOCATION 38 INSTRUMENTATION

The emissions measurements were made using analytical instruments and equipment contained in a KVB owned mobile laboratory. Gaseous emission measurements were made with the following analytical instruments:

Emission Species	Manufacturer	Measurement Method	Model No.
Hydrocarbon	Beckman Instruments	Flame Ionization	402
Carbon Monoxide	Beckman Instruments	IR Spectrometer	865
Oxygen	Teledyne	Polarographic	326A
Carbon Dioxide	Beckman Instruments	IR Spectrometer	864
Nitrogen Oxides	Thermo Electron	Chemiluminescent	10A

These instruments were described in detail in the previous paragraphs.

TABLE 2-1. TRACE SPECIES AND ORGANICS TO BE IDENTIFIED

Elements

Antimony
Arsenic
Barium
Beryllium
Cadmium
Calcium
Chlorine
Chromium
Cobalt
Copper
Fluorine
Iron
Lead
Manganese
Mercury
Nickel
Selenium
Tellurium
Tin
Titanium
Vanadium
Zinc

Species

Total sulfates
Total nitrates

Organics

Total polychlorinated biphenyls (PCB)
Total polycyclic organic matter (POM)
Specific POM compounds:
  7, 12 - dimethylbenz (a) anthracene
  Dibenz (a,h) anthracene
  Benzo (c) phenanthrene
  3-Methylcholanthrene
  Benzo (a) pyrene
  Dibenzo (a,h) pyrene
  Dibenzo (a,i) pyrene
  Dibenzo (c,g) carbazole

Total oxides of sulfur were measured by wet chemistry methods using the sampling train and analytical procedure of the Shell-Emeryville method. Sulfur oxides were measured only during the #6 oil tests. Total particulate measurements were made using an EPA Method 5 sampling train. Particulate size distribution was made using a cascade impactor manufactured by Meteorology Research, Inc.

2.3 LOCATION 19 EQUIPMENT CHARACTERISTICS

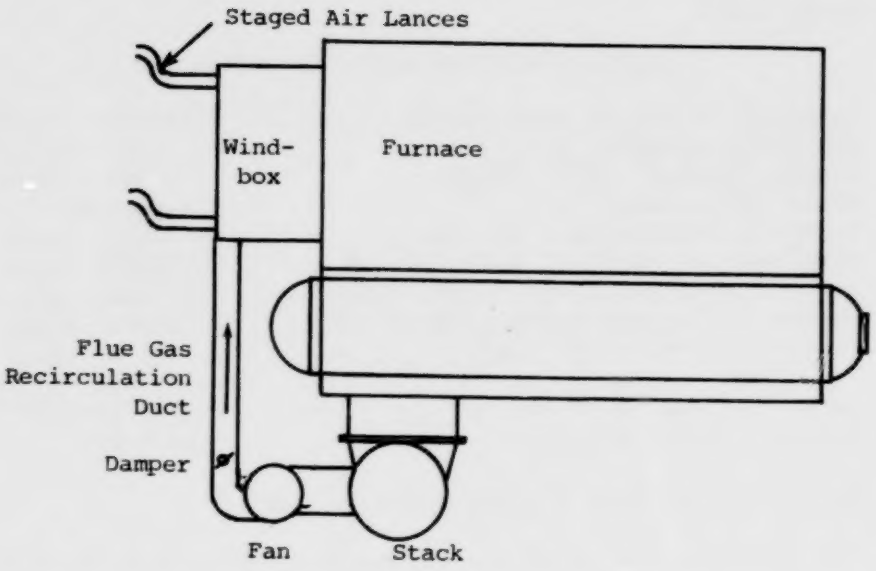
The test unit used to evaluate the combustion modifications at Location 19 was a Type DS two drum watertube package steam generator, rated at a heat output of 5.1 MW (17500 lb/h of steam flow), designed for pressurized furnace operation. The unit has been modified to incorporate staged combustion air and flue gas recirculation. A schematic of the boiler is shown in Figure 2-4.

Staged combustion air was introduced into the furnace through four 3 inch pipe size diameter lances. Insertion depth of the lances was variable up to 2.1 m (7 ft). Staged combustion air was supplied by a separate blower and flow rate was adjusted by dampers in each supply line.

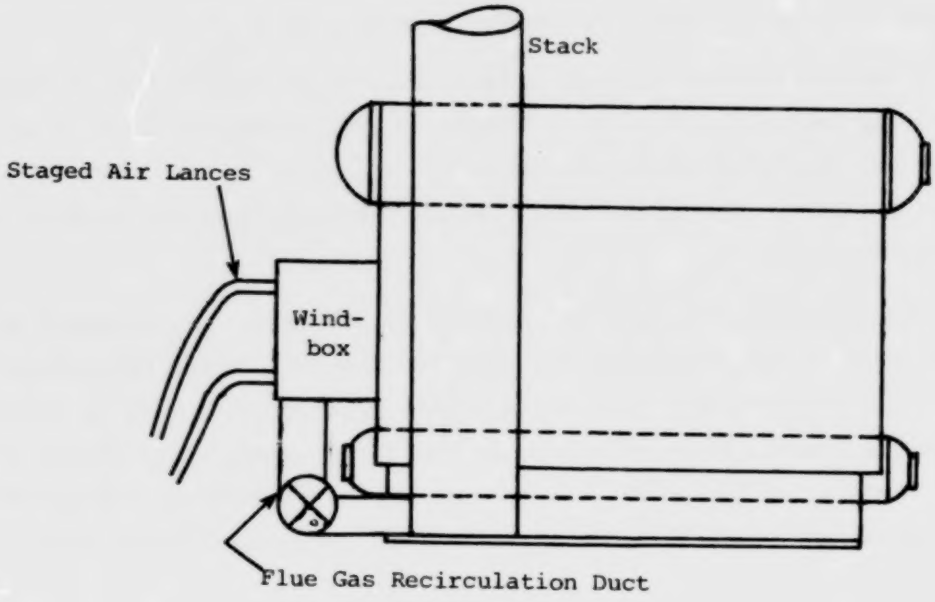
A new burner windbox was designed and fabricated for incorporating flue gas recirculation into the system. Flue gas was extracted from the base of the stack by means of a blower and ducted to the burner windbox via an insulated 14" duct. The flue gas was injected into the burner from a plenum at the rear of the windbox.

The flue gas is recirculated to the burner by withdrawing the gas from the base of the stack ($T_{gas} \sim 545$ K) with a high temperature fan. The high temperature gas is ducted to the burner windbox through an insulated duct containing a calibrated flat plate orifice for measuring flow. The burner windbox has been modified to inject the flue gas radially inward through an adjustable slot at the rear of the burner.

Staged combustion is accomplished by injecting air into the combustion zone through four probes oriented 90 deg apart around the burner. These staged air probes are 76.2 mm (3 in.) diameter and are adjustable in length up to 2.1 m (7 ft). The ends of the probes are blocked and slots machined in the pipe to inject the air radially inward toward the flame centerline.



(a) Top View



(b) Side View

Figure 2-4. Schematic diagram of staged air and flue gas recirculation system installed at Location 19.

The capacity and design conditions of the boiler are presented in the following table.

Location 19, Steam Boiler Specifications

Pounds of steam per hour (kg/s)	17,500 (2.206)
Operating pressure, psig (kPa)	160 (1207)
Design pressure, psig (kPa)	250 (1827)
Steam temperature	saturated
Feedwater temperature, °F (K)	220 (377)
Total heating surface, sq ft (m^2)	1,881 (175)
Radiant heating surface, sq ft (m^2)	288 (27)
Convection heating surface, sq ft (m^2)	1,593 (148)
Furnace volume, cu ft (m^3)	430 (12)
Fuel Type	natural gas, #2 oil, #6 oil
Furnace length ft., (m)	9' - 10-13/16" (3.018)
Furnace width ft., (m)	5' - 10" (1.778)

Special Instrumentation Requirements

The Location 19 test boiler was modified to incorporate staged combustion air and flue gas recirculation. As a consequence of these modifications, additional instrumentation was required to measure the staged combustion air flow and the recirculated flue gas flow.

Staged combustion air was introduced into the boiler through four lances on the face of the boiler. To measure the staged air flow, a set of curves was generated which give secondary air flow as a function of lance injection pressure. The lance injection pressure was then measured for all staged air tests.

Recirculated flue gas was measured by installing a calibrated sharp-edged orifice in the duct which returned the flue gas to the combustion air plenum. The pressure drop across the orifice was measured with an inclined manometer as was the static pressure in the duct. Temperature of the flue gas was measured at the orifice inlet with a high temperature thermometer. All pertinent data were recorded for each flue gas recirculation test.

2.4 LOCATION 38 EQUIPMENT CHARACTERISTICS

The test boiler at Location 38 was a vertical watertube type rated at 5.67 kg/s (45,000 lb/hr) of saturated steam flow. The unit was modified to incorporate sidefire air capability. It had a single burner that fired either natural gas or #6 fuel oil. The boiler was also equipped with an air preheater which can raise the combustion air temperature to a maximum of 450 K (350 °F).

The sidefire installation is shown schematically in Figure 2-5. A 36 cm diameter manifold was run along each side of the boiler and was connected to a fan mounted on the floor at the rear of the boiler. Flexible pipes connected the manifold to the overfire air ports in the furnace side walls.

The amount of sidefire air going to each downcomer was controlled by butterfly valves installed in each of the two legs of the manifold and in the upper section of each downcomer.

Staged combustion air tests were conducted on this unit with both natural gas and #6 oil firing. During the staged air tests the amount and location of the injection of the sidefire air addition was systematically varied while the total amount of combustion air was held constant.

Location 38, Steam Boiler Specifications

Pounds of steam per hour (kg/s)	45,000	(5.67)
Operating pressure, psig (kPa)	140	(1070)
Design pressure, psig (kPa)	250	(1830)
Steam temperature, °F (K)	360	(456)
Feedwater temperature, °F (K)	275	(408)
Furnace volume, cu. ft. (m^3)	1,537	(43.5)
Fuel type	natural gas, No. 6 oil	
Furnace length, ft. (m)	10'-6"	(3.2)
Furnace width, ft. (m)	12'	(3.7)
Maximum air temperature, °F (K)	350	(450)

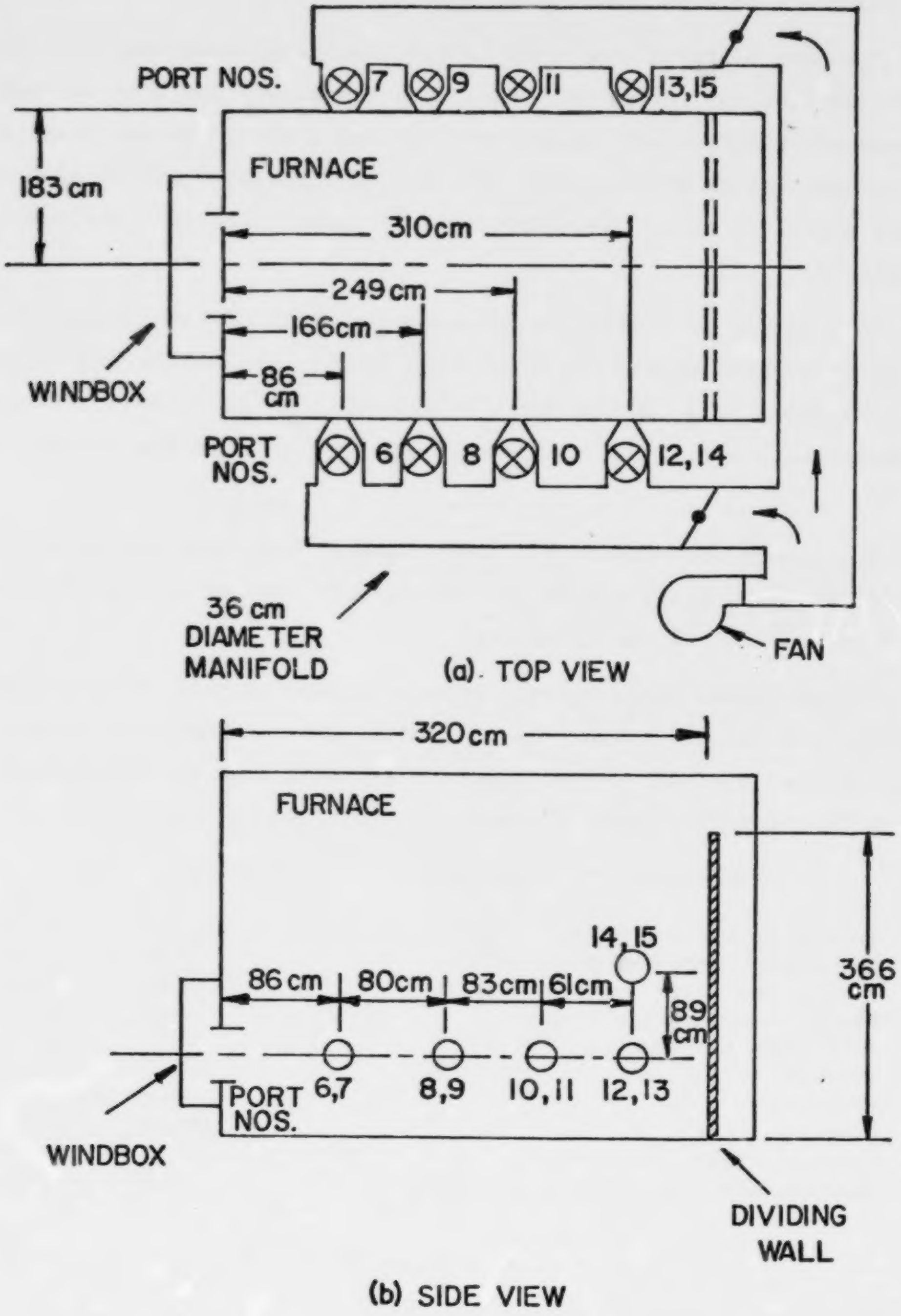


Figure 2-5. Schematic diagram of staged air system installed at Location 38.

SECTION 3.0

TEST RESULTS

This section summarizes the emission and efficiency data collected on the Location 19 and 38 watertube boilers. The Location 19 boiler was modified to incorporate staged combustion air, flue gas recirculation and combinations of these. At Location 19 the boiler was tested with natural gas, #2 and #6 fuel oils. The Location 38 boiler had capability for staged combustion air and variable combustion air preheat. Tests were conducted with natural gas and #6 fuel oil. The results presented herein summarize the gaseous and particulate emissions data, efficiency and conclusions, for various combustion modifications.

3.1 LOCATION 19 TEST RESULTS

3.1.1 Location 19 Baseline Tests

Baseline measurements were made with the boiler in the "as found" condition firing #2 oil, #6 oil, and natural gas. Baseline measurements were made at the start of each group of combustion modification tests and when the boiler fuel was changed. The boiler load for baseline and all combustion modification tests was approximately 80% of rated capacity.

Complete baseline emissions data on each fuel are included in Table 3-1, which summarizes the emissions data from those tests during which particulate, particulate size distribution or SO_x were measured. This table includes baseline data and data at each of the modified boiler conditions. Particulate, particulate size distribution, and SO_x measurements were made only at the optimum low NO_x condition for each combustion modification or combination of modifications. These data were not measured during the parametric tests for each modification and the emissions data for the parametric tests are not tabulated in Table 3-1.

TABLE 3-1. SUMMARY OF MODIFIED BOILER TESTS

Test Run	Date 1977	Nominal Steam Load Mg/hr	Fuel	O_2 %	CO_2 %	NO_x* ng/J (ppm)	NO* ng/J (ppm)	HC* ng/J (ppm)	CO* ng/J (ppm)	SO_2* ng/J (ppm)	Wet Chemistry SO_2* ng/J (ppm)	Wet Chemistry SO_3* ng/J (ppm)
19-5	1-6	6.58	#2	3.20	13.5^+	67.4 (120)	67.4 (120)	0.4 (2)	1.4 (4)	62.8 (80)	76.3 (90)	1 (1.1)
19-7	1-6	6.35	#2	2.95	13.2^+	64.6 (115)	64.6 (115)	1.2 (6)	4.1 (12)	95.8 (113)	--	--
19-74	1-19	6.58	#2	1.15	14.6^+	54.5 (97)	54.5 (97)	0.6 (3)	61.7 (181)	70.3 (90)	99.2 (127)	3 (3)
19-76	1-19	6.58	#2	1.08	14.6^+	54.5 (97)	54.5 (97)	0.6 (3)	61.7 (181)	74.2 (95)	--	--
19-83	1-20	6.58	#2	0.85	14.8^+	17.4 (31)	17.4 (31)	1.0 (5)	7.2 (21)	71.1 (91)	71.1 (91)	5 (5)
19-85	1-20	6.62	#2	0.68	14.9^+	18.5 (33)	18.5 (33)	0.8 (4)	24.2 (71)	65.6 (84)	--	--
19-116	1-26	6.58	#2	3.10	13.0^+	54.0 (96)	54.0 (96)	1.2 (6)	11.9 (35)	73.4 (94)	67.2 (86)	1 (1)
19-117	1-26	6.62	#2	3.18	13.0^+	55.1 (98)	55.1 (98)	0	8.2 (24)	82.8 (106)	--	--
19-179	3-3	6.49	#2	3.5	13.2	18.0 (32)	18.0 (32)	0	6.1 (18)	76.5 (98)	78.9 (101)	7 (9)
19-97	1-24	6.26	#6	3.00	13.6^+	120.3 (214)	120.3 (214)	2.1 (11)	1.4 (4)	256.4 (329)	245 (314)	4 (4)
19-99	1-24	6.35	#6	3.10	13.6^+	123.1 (219)	123.1 (219)	1.2 (6)	1.4 (4)	277.2 (355)	--	--
19-132	2-17	6.44	#6	0.98	15.2^+	84.3 (150)	83.7 (149)	3.7 (19)	62.4 (183)	305.4 (391)	316.3 (405)	3 (4)
19-143	2-21	6.24	#6	3.1	13.6^+	84.9 (151)	83.7 (149)	1.2 (6)	8.2 (24)	269.4 (345)	280.4 (359)	3 (4)
19-159	2-23	6.35	#6	1.75	14.5^+	84.3 (150)	84.3 (150)	1.2 (6)	30.7 (90)	293.6 (376)	266.9 (329)	2 (2)
19-170	3-1	6.49	#6	4.2	13.2^+	90.5 (161)	90.5 (161)	0	9.2 (27)	289.0 (370)	279.6 (358)	6 (7)
19-147	2-22	6.59	NG	3.03	10.2	48.5 (95)	48.5 (95)	0.7 (4)	1.2 (4)	0	--	--
19-171	3-2	6.36	NG	3.2	10.6	12.2 (24)	12.2 (24)	0.5 (3)	6.2 (20)	0	--	--
19-177	3-2	6.82	NG	2.5	10.6	11.2 (22)	11.2 (22)	0	5 (16)	0	--	--
19-181	3-4	6.27	NG	3.2	11.0	45.9 (90)	45.9 (90)	0.9 (5)	5.9 (19)	0	--	--
19-184	3-4	6.32	NG	1.1	12.0	44.4 (87)	44.4 (87)	0	308 (995)	0	--	--
19-186	3-4	6.59	NG	2.8	11.0	25.0 (49)	25.0 (49)	0	90.7 (293)	0	--	--
19-188	3-4	6.23	NG	4.8	9.7	11.2 (22)	11.2 (22)	0	4.0 (13)	0	--	--
19-190	3-7	6.29	NG	3.25	10.3	13.3 (26)	13.3 (26)	0	5.0 (16)	17.7 (25)	33.3 (47)	2 (3)
19-193	3-8	6.49	NG	3.3	10.5	42.3 (83)	42.3 (83)	0.2 (1)	7.1 (23)	--	--	--

(continued)

*Corrected to 3% O_2

$^+$Calculated from fuel analysis

TABLE 3-1 (continued).

Test Run	Fuel	Total Partic. ng/J (lb/MMB)	Solid Partic. ng/J (lb/MMB)	Stack Temp. K (°F)	Eff. %	Smoke Spot	FGR %	Opacity %	ϕ_B	Lance Depth m (ft)	Comments
19-5	#2	24.24 (0.0564)	2.545 (0.006)	542 (516)	82.4	0	--	0	--	--	Baseline - particulate test
19-7	#2	--	--	539 (511)	82.6	0	--	0	--	--	Baseline - Cascade impactor
19-74	#2	16.29 (0.0379)	5.95 (0.0138)	545 (521)	83.4	5	--	0	--	--	Low O_2 particulate
19-76	#2	--		545 (521)	83.3	4.5	--	0	--	--	Low O_2 - Cascade impactor
19-83	#2	5.84 (0.0136)	1.95 (0.0045)	578 (581)	81.7	0	28.4	0	--	--	FGR, Low O_2, Particulate
19-85	#2	--		579 (582)	81.8	0	27.9	0	--	--	FGR, Low O_2, Particulate
19-116	#2	11.6 (0.0270)	9.01 (0.0210)	544 (520)	82.4	4	--	13	1.04	1.8 (6)	Staged air - Particulate
19-117	#2	--		542 (516)	82.5	5.5	--	13	1.04	1.8 (6)	Staged air - Cascade impactor
19-179	#2	4.16 (0.0097)	3.31 (0.0077)	564 (555)	81.3	0	26.3	0	1.10	1.2 (4)	FGR & SA - Low O_2, Cascade impactor, Particulate
19-97	#6	36.21 (0.084)	27.55 (0.064)	539 (511)	82.8	0.5	--	0	--	--	Baseline - Particulate
19-99	#6	--		543 (517)	82.6	0	--	0	--	--	Baseline - Cascade impactor
19-132	#6	28.87 (0.067)	25.80 (0.060)	519 (475)	83.8	2.5	--	6	--	--	Low O_2 - Particulate
19-143	#6	31.80 (0.074)	27.20 (0.064)	526 (487)	82.9	2.5	--	22	1.03	1.5 (5)	Staged Air, Particulate
19-159	#6	32.32 (0.075)	29.36 (0.068)	548 (526)	82.1	1.5	24.7	0	--	--	Max. FGR, Particulate
19-170	#6	26.79 (0.067)	9.10 (0.021)	544 (579)	80.7	1.5	23.1	0	1.01	1.2 (4)	FGR & SA, Particulate
19-147	NG	--	--	554 (538)	77.8	--	0	0	--	--	Baseline ring burner
19-171	NG	--	--	561 (550)	77.3	--	20.3	0	--	--	Max. FGR, Gas gun burner
19-177	NG	--	--	541 (557)	77.5	--	19.9	0	--	--	Max. FGR, Low O_2, Gas gun burner
19-181	NG	--	--	538 (508)	78.2	--	--	0	--	--	Baseline, Gas gun burner
19-184	NG	--	--	527 (489)	79.1	--	--	0	--	--	Minimum O_2, Gas gun burner
19-186	NG	--	--	534 (501)	78.8	--	--	0	0.97	2.1 (7)	Max. SCA, lance at 7'
19-188	NG	--	--	550 (530)	76.9	--	17.8	0	0.86	2.1 (7)	FGR & SCA - Normal O_2
19-190	NG	2.63 (0.0061)	1.67 (0.0039)	555 (539)	77.6	--	17.2	0	--	--	Max. FGR, Particulate
19-193	NG	3.68 (0.0086)	1.92 (0.0045)	541 (514)	78.3	--	0	0	--	--	Baseline - Particulate

The measured baseline NO_x emissions with the boiler firing #2 oil were 65.8 ng/J (117 ppm). With the unit firing #6 oil, baseline NO_x emissions were 121.7 ng/J (216 ppm). Baseline NO_x emissions with natural gas were 42.3 ng/J (83 ppm).

Baseline particulate measurements were made with the boiler firing #2 oil, #6 oil and natural gas. With #2 oil, the total particulate was 24.24 ng/J (0.0564 lb/MMBtu) and the solid particulate was 2.595 ng/J (0.0060 lb/MMBtu). Number 6 oil baseline particulate measurements were 36.21 ng/J (0.084 lb/MMBtu) total particulate and 27.55 ng/J (0.064 lb/MMBtu) solid particulate. When firing natural gas, the total particulate measured 3.68 ng/J (0.0086 lb/MMBtu) and solid particulate measured 1.92 ng/J (0.0045 lb/MMBtu).

During this test program, combustion modifications were evaluated using all three fuels. Oil samples were taken periodically during the test program and sent to an independent testing laboratory for analysis. A natural gas sample was also taken during the testing and submitted for analysis. A summary of fuel properties is presented in Tables 3-2 and 3-3 for oil and natural gas respectively.

3.1.2 Location 19 Combustion Modifications With #2 Oil

Combustion modification testing with the unit operating on #2 oil consisted of excess air variation, staged combustion, flue gas recirculation, and combinations of staged air and flue gas recirculation.

Excess Oxygen--

The effect of excess oxygen on NO_x emissions was evaluated by Tests 1, 11, 12, and 13. These data are presented in Figure 3-1. Reducing excess O_2 resulted in a decrease of 2.7 ng/J (0.0063 lb/MMBtu) per % O_2.

TABLE 3-2. SUMMARY OF LOCATION 19 FUEL OIL ANALYSES

Fuel Date Laboratory No.	#2 Oil 1/6/77 13520	#2 Oil 1/10/77 13520	#2 Oil 1/19/77 14009	#6 Oil 12/15/76 13042	#6 Oil 1/19/77 14009	#6 Oil 2/16/77 14667	#6 Oil 3/2/77 14667	#6 Oil 3/10/77 16554	#6 Oil 3/17/77 16554	#6 Oil 3/21/77 16554	#6 Oil 3/23/77 16554
Carbon, %	86.45	85.62	86.49	87.55	86.91	87.55	87.30	87.23	86.06	86.25	86.55
Hydrogen, %	13.01	12.99	13.17	11.49	11.78	11.40	11.34	11.34	11.11	11.25	11.26
Nitrogen, %	<0.001	<0.001	0.008	0.20	0.20	0.23	0.22	0.23	0.32	0.32	0.30
Sulfur, %	0.16	0.10	0.14	0.56	0.54	0.60	0.60	0.55	1.17	1.18	1.02
Ash, %	<0.001	<0.001	0.001	0.020	0.019	0.034	0.026	0.027	0.025	0.024	0.025
Oxygen, %	0.38	1.09	0.19	0.18	0.55	0.19	0.51	0.62	1.32	0.98	0.85
API Gravity	37.8	37.7	37.5	20.7	20.7	17.0	17.3	17.5	14.3	15.7	15.8
HHV, Btu/lb	19,680	19,680	19,610	18,910	19,000	18,780	18,850	18,850	18,670	18,740	18,750
HHV, kJ/kg	45,775	45,775	45,613	43,984	44,194	43,682	43,845	43,845	43,426	43,589	43,613

TABLE 3-3. LOCATION 19 NATURAL GAS ANALYSIS

Date	3/7/77
Laboratory No.	14781
Oxygen, %	<0.009
Nitrogen, %	0.29
Carbon dioxide, %	0.54
Methane	95.84
C 2	2.92
C 3	0.22
C 4	0.099
C 5	0.039
C 6 plus	0.054
Heating value, Btu/SCF (dry)	1035

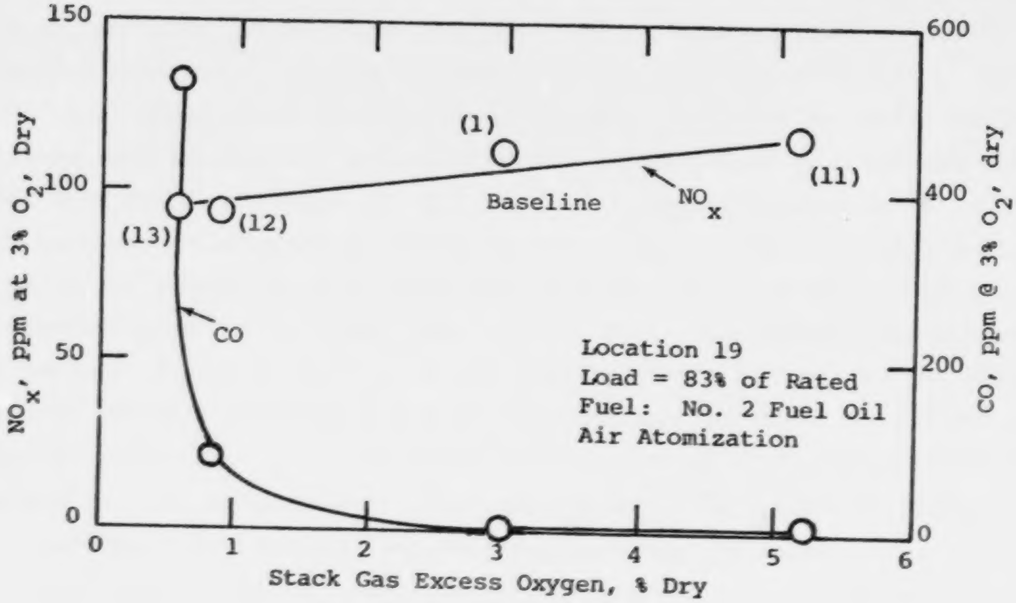


Figure 3-1. The effect of excess oxygen on NO$_x$ emissions (No. 2 oil)

Staged Combustion Air--

For the staged air tests, the depth of the lances which supplied the staged air was varied from 1.2 to 2.1 m (4 to 7 ft) and the ratio of burner-to-staged combustion air was changed. Total furnace length is 3.0 m (9.9 ft). The effect of staged combustion air injection point on NO_x emissions is presented in Figure 3-2 for the unit operating on #2 oil. These data indicate that the effect of injection distance is very slight beyond about 1.2 m (4 ft) and the more fuel rich the burner operates, the greater the reduction in NO_x. At an injection depth of 1.2 m, the NO_x was reduced 27% from the baseline condition and increasing the injection point to 2.1 m resulted in a reduction of 30% from the baseline condition, with the burner operating at 91% of the theoretical air ($\phi = 1.1$). The symbol ϕ is the equivalence ratio, defined as the ratio of stoichiometric air-fuel ratio to actual air-fuel ratio. With the burner operating at approximately the theoretical air-fuel ratio, the reduction is only 15.5% at an injection depth of 2.1 m. The effect of lowering the overall excess air with staged combustion is also shown in this figure. A reduction of 44% in NO_x was measured with the lance at 2.1 m and the burner operating at 91% theoretical air while the overall O_2 level was reduced from 3% O_2 to 2.6%.

Flue Gas Recirculation--

The influence of flue gas recirculation on NO_x emissions was evaluated at two excess O_2 conditions. Tests were conducted at a nominal O_2 of approximately 3% and a low O_2 condition of approximately 1%. The test results are presented in Figure 3-3. At the nominal O_2 condition (∿ 3%), flue gas recirculation results in a decrease in NO_x of 68% for the maximum recirculation rate of 23.6%. Even the low recirculation rate of 14.7% results in a decrease in NO_x of 52%. With the boiler operating in the low O_2 condition, the maximum recirculation rate of 26.5% resulted in a reduction in NO_x of 71% and the minimum recirculation rate of 15% gave a 58% reduction in NO_x.

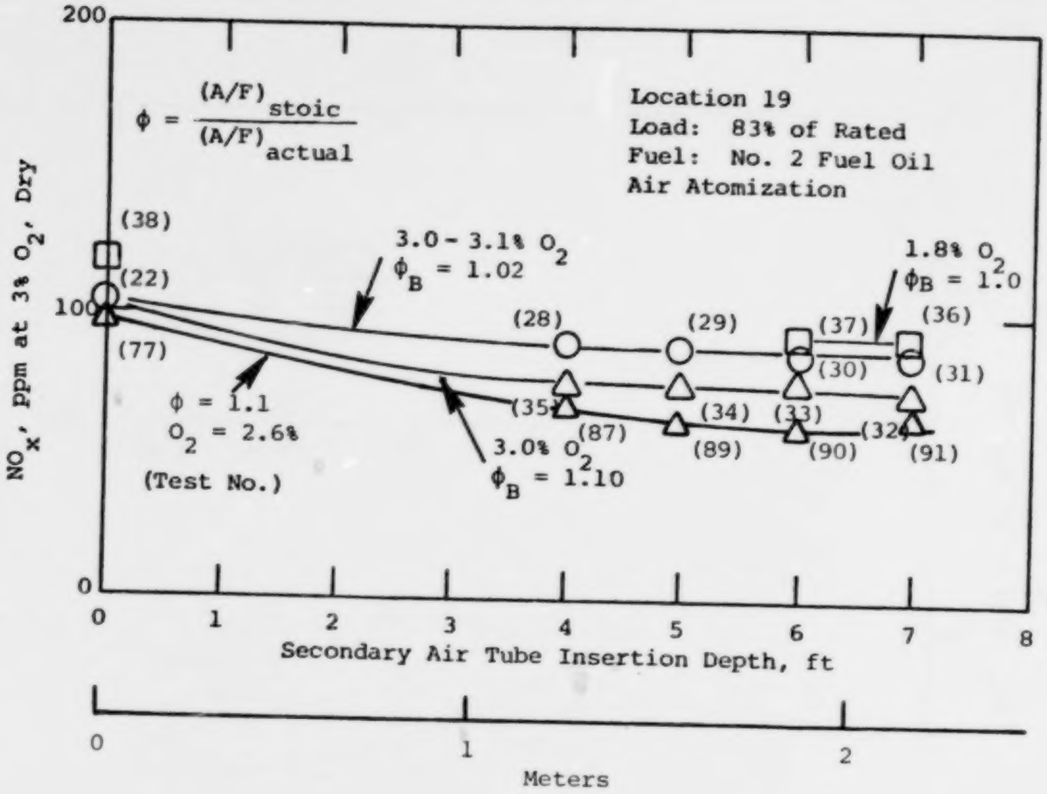


Figure 3-2. NO_x emissions as a function of staged air injection depth and burner air (#2 oil).

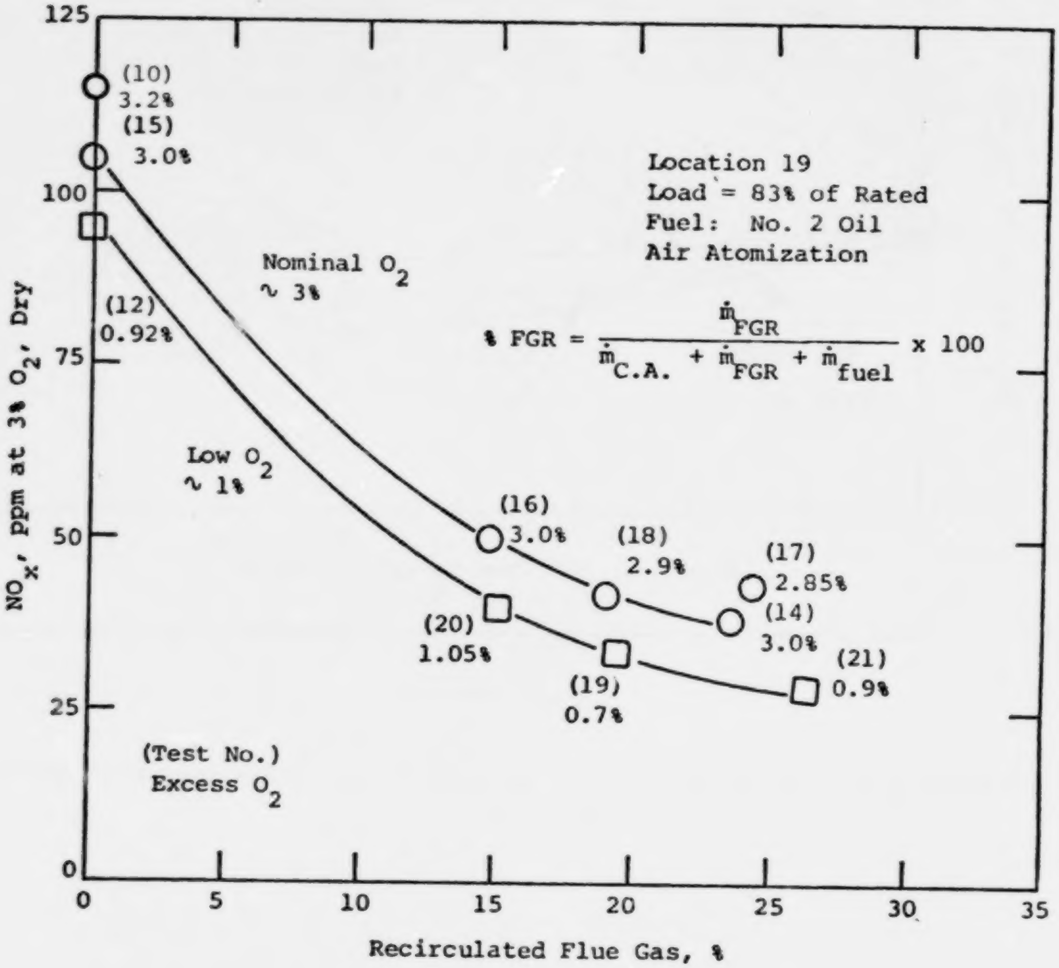


Figure 3-3. NO_x emissions as a function of percent flue gas recirculation (No. 2 oil).

Flue Gas Recirculation and Staged Combustion Air--

Tests were conducted to evaluate the effect of flue gas recirculation in combination with staged combustion air. NO_x as a function of flue gas recirculation rate is presented in Figures 3-4 and 3-5 for staged air injection depths of 1.2 m and 2.1 m respectively. NO_x reductions of 77% and 73% were demonstrated using both maximum flue gas recirculation and staged air at 1.2 m and 2.1 m injection depth respectively with the boiler in the low O_2 operating mode. This is a slightly greater reduction in NO_x than realized by flue gas recirculation alone. The combination of FGR and staged combustion with the boiler in the normal O_2 mode resulted in a 69% reduction in NO_x.

3.1.3 Combustion Modifications With #6 Oil

Combustion modification testing with the unit operating on #6 oil consisted of excess air variation, staged combustion, flue gas recirculation and combinations of flue gas recirculation and staged air.

Excess Oxygen--

The effect of excess air on NO_x emissions for #6 oil firing is shown in Figure 3-6. Excess O_2 was varied over a range of 0.7% to 5.2%. Lowering the O_2 level to 0.7% resulted in a 30% decrease in NO_x from the baseline condition. The overall effect of O_2 on NO_x emissions is 11.1 ng/J (0.026 lb/MMBtu) decrease in NO per percent decrease in excess O_2.

Staged Combustion Air--

During this test series staged combustion air injection depths were varied. The results are shown in Figure 3-7. As in the case of #2 oil combustion, little effect on NO_x was detected beyond 1.2 m insertion depth but the effect of burner equivalence ratio (ϕ) is more pronounced. At the normal O_2 condition ($\sim$ 3.1% O_2), changing the burner air from slightly air rich ($\phi_B \sim 0.96$) to slightly fuel rich ($\phi_B > 1$) resulted in a NO_x emission reduction of about 13%. Lowering the overall O_2 level to 1.9% while maintaining the burner in the fuel-rich condition resulted in an additional decrease of 14%. These reductions are both relative to the staged combustion condition with the lance depth set at 2.1 m. Relative to the baseline condition, the reductions are: 19% for normal O_2, burner slightly air rich; 29% for normal O_2, burner slightly fuel rich; and 42% for low O_2, burner slightly fuel rich.

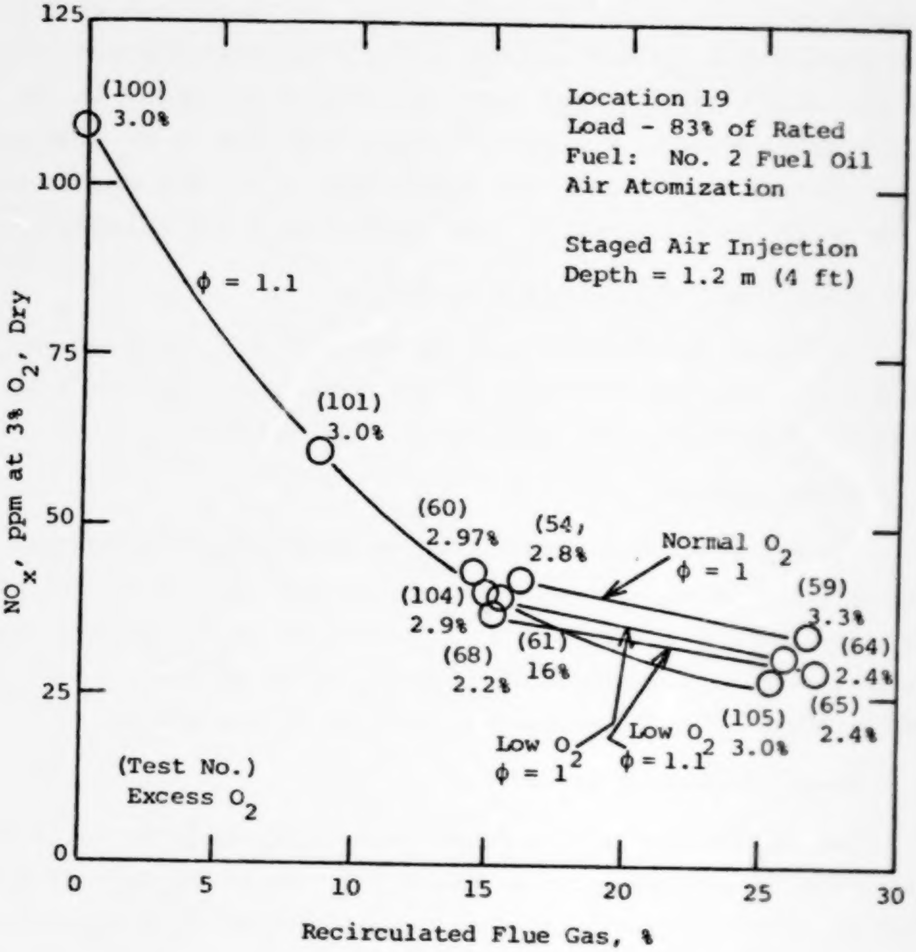


Figure 3-4. NO$_x$ emissions as a function of combined flue gas recirculation and staged air at 1.2 m (No. 2 oil).

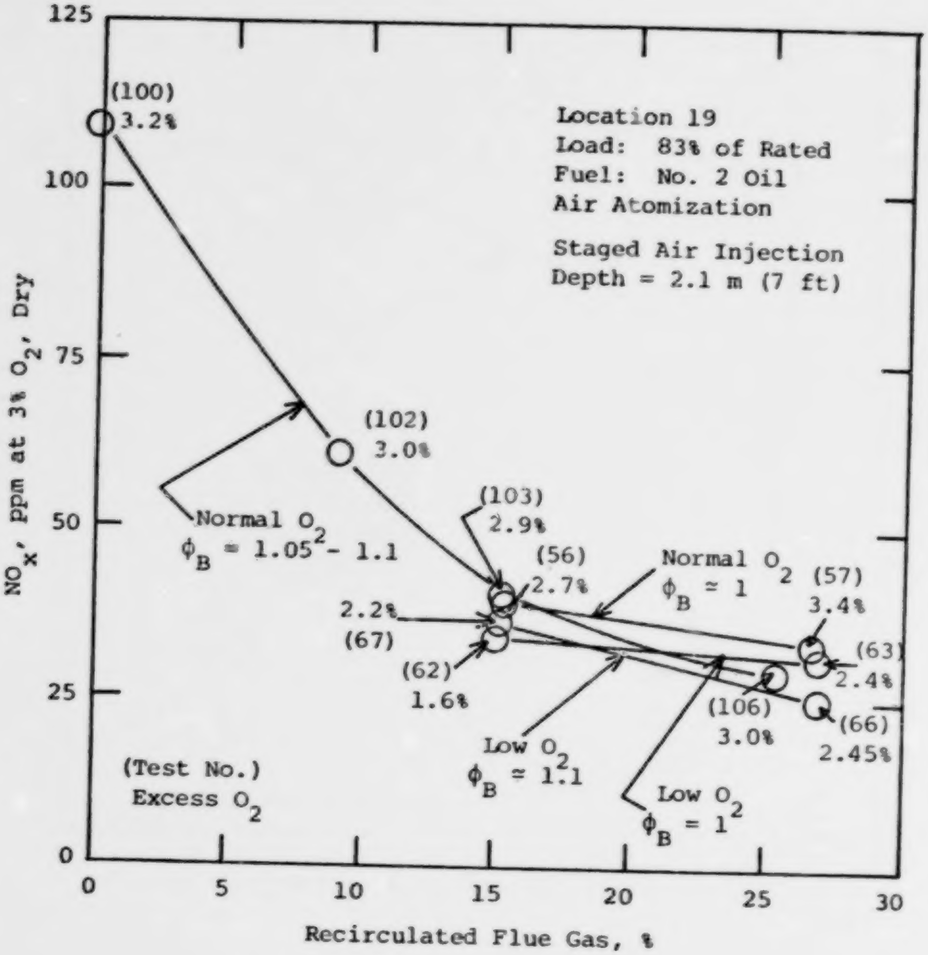


Figure 3-5. NO_x emissions as a function of combined flue gas recirculation rate and staged air at 2.1 m (7 ft).

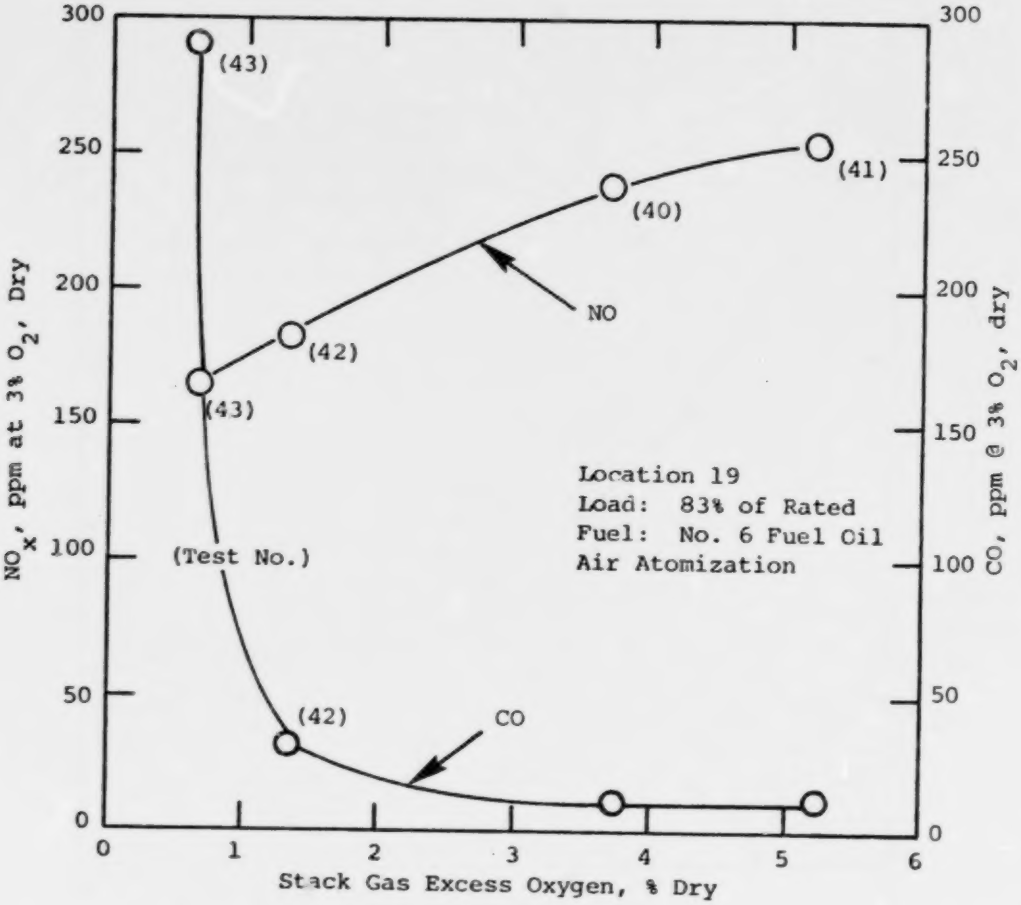


Figure 3-6. The effect of excess oxygen on NO_x emissions (No. 6 oil).

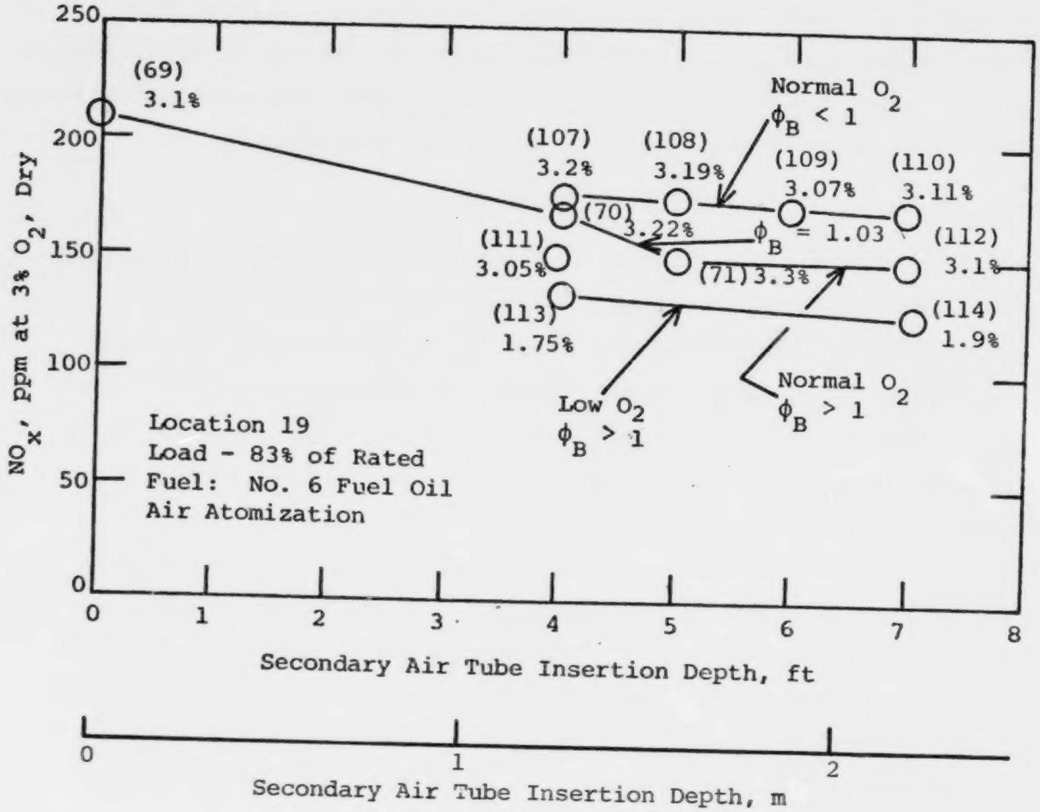


Figure 3-7. NO$_x$ emissions as a function of staged air injection depth and burner air (#6 oil).

Flue Gas Recirculation--

Flue gas recirculation tests with #6 oil were conducted with the boiler operating in the normal and low O_2 conditions. The data from these tests are presented in Figure 3-8. Flue gas recirculation rates were varied from 13.8% to 23.3% at the normal O_2 condition and from 14.4% to 25.8% at the low O_2 condition. With the unit operating at normal O_2 levels, flue gas recirculation resulted in an 11% decrease while at the low O_2 conditions, a 40% reduction in NO_x was realized. Both of these reductions were accomplished at the maximum recirculation rates of 23.3 and 25.8% respectively.

Flue Gas Recirculation and Staged Combustion Air--

The effect of flue gas recirculation combined with staged combustion air was determined for the boiler firing #6 oil. The combined operation tests were conducted at nominal and low excess C_2 conditions and at staged air injection depths of 1.2 and 2.1 m. Figure 3-9 shows the effect of flue gas recirculation rate on NO_x emissions at the nominal, high and low excess O_2 conditions with staged air injection at 1.2 m. The maximum reduction in NO_x occurred with the excess O_2 at 1.5% and 19.6% flue gas recirculation. The NO_x was reduced 50% relative to the normal baseline at this operating condition. Figure 3-10 shows the same data but with an injection depth of 2.1 m. The maximum reduction at this condition is 53% relative to the baseline condition. The effect of burner equivalence ratio, ϕ, is also shown in Figures 3-9 and 3-10. At 2.1 m injection depth, changing the equivalence ratio from approximately 1 (stoichiometric A/F) to 1.1 (fuel rich) changes the NO_x reduction from 36% to 53%.

3.1.4 Combustion Modifications With Natural Gas

Combustion modification testing with the unit operating on natural gas consisted of excess air variations, staged combustion, flue gas recirculation and combinations of flue gas recirculation and staged air. The original ring gas burner was replaced with a gas gun because of flame stability problems when flue gas recirculation was incorporated.

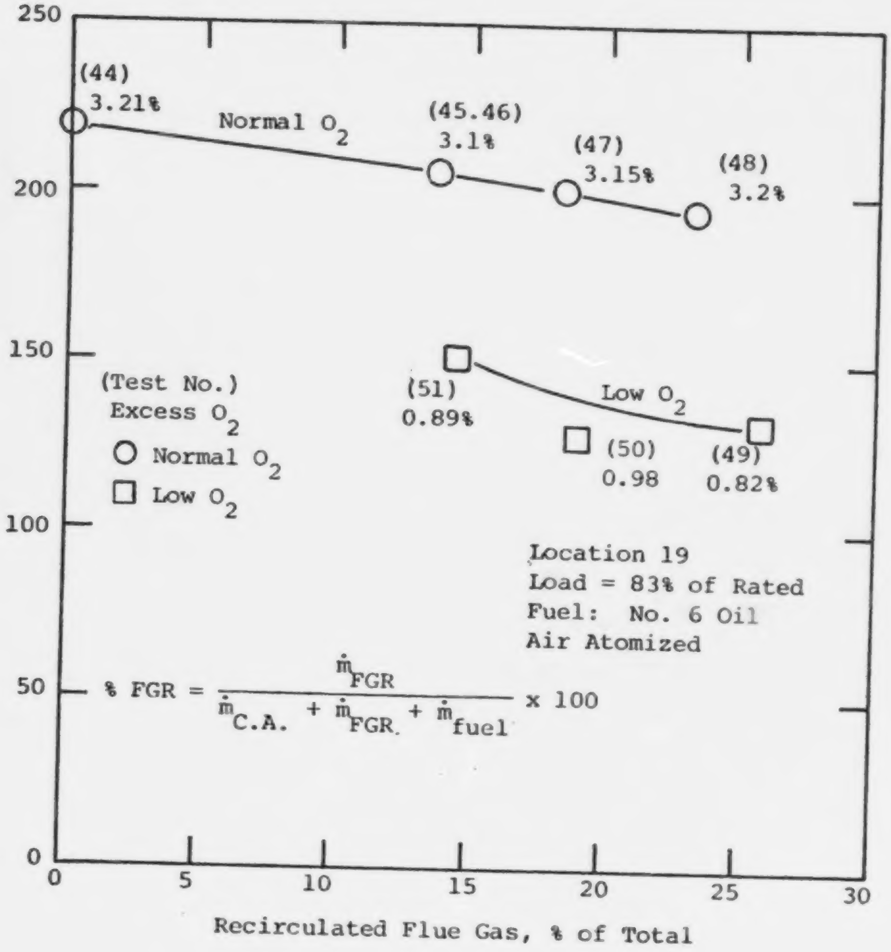


Figure 3-8. The effect of flue gas recirculation on NO_x emissions (No. 6 oil).

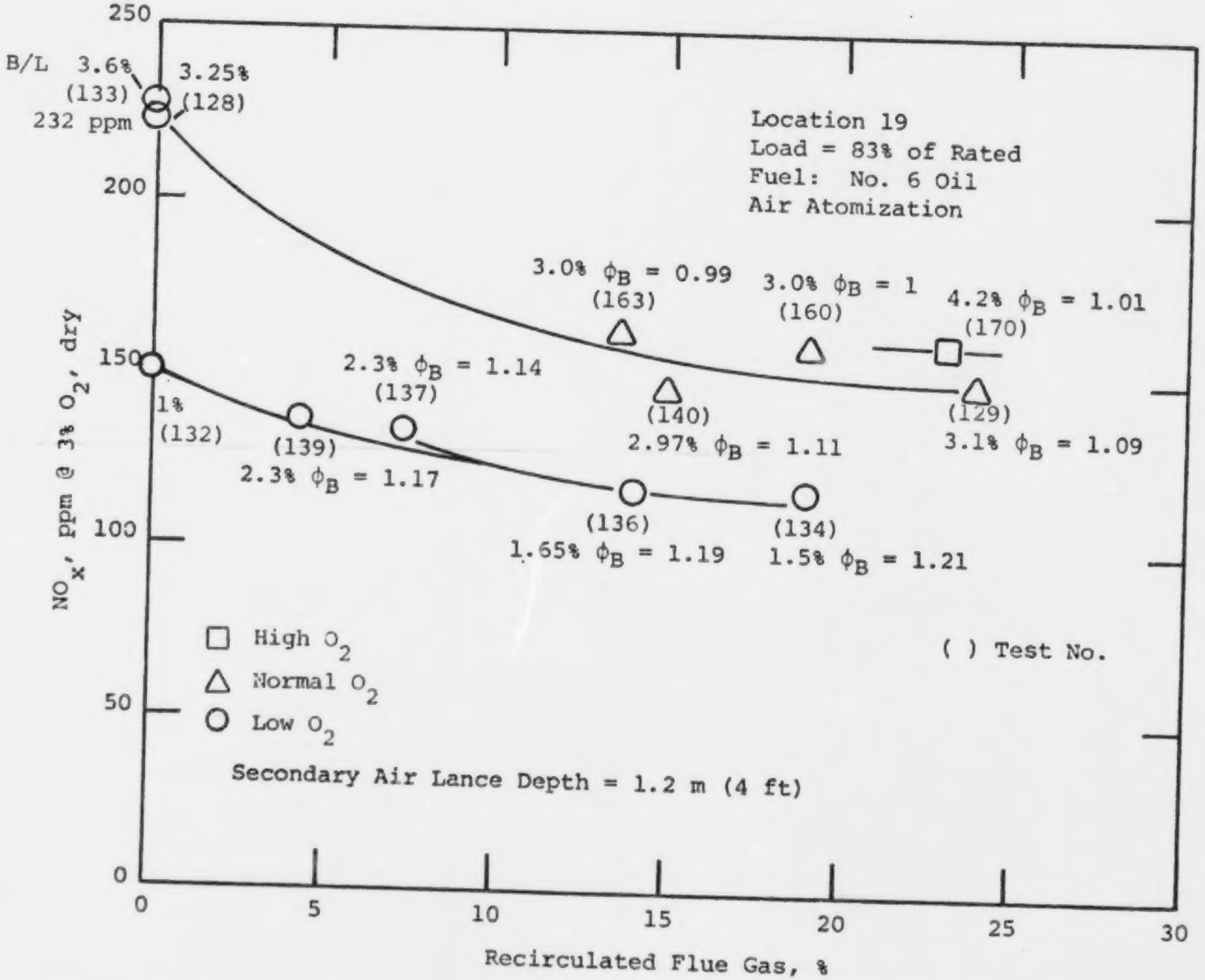


Figure 3-9. The effect of combined flue gas recirculation and staged combustion air at 1.2 m on NO$_x$ emissions (#6 oil).

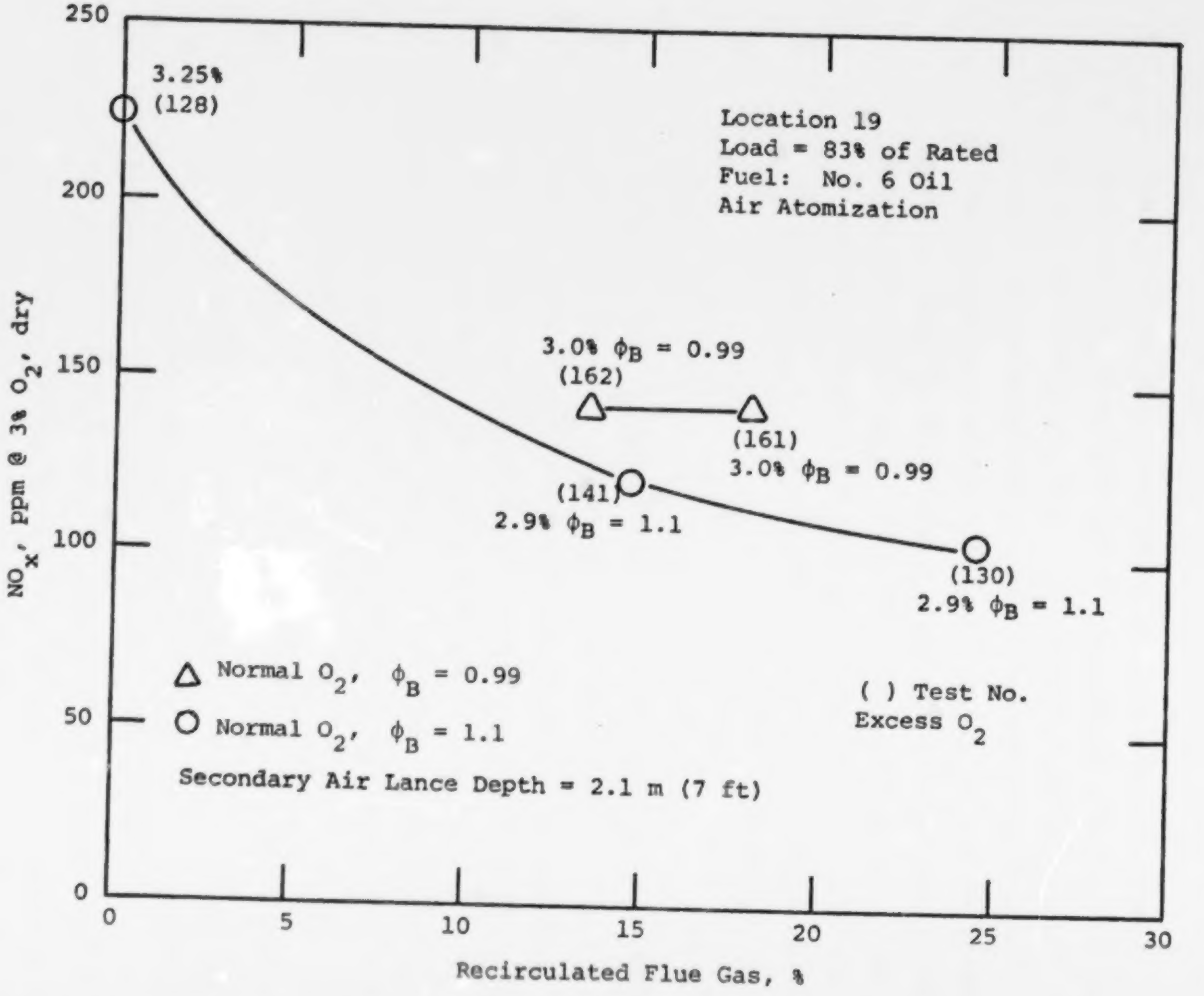


Figure 3-10. The effect of combined flue gas recirculation and staged combustion air at 2.1 m on NO_x emissions (#6 oil).

Excess Oxygen--

Figure 3-11 presents the test results of NO_x variation versus excess O_2 variation with the natural gas gun burner. These data show that reducing the excess O_2 level from the baseline condition of 3.2%, to 2.0%, resulted in an increase in NO_x emissions of approximately 2%. Diminishing the O_2 level further, to 1.1%, decreased the NO_x by 3% from the baseline condition. The lower limit of excess O_2 was determined to be approximately 1% based on the effect of O_2 on CO emissions as shown in Figure 3-12. This figure shows that below about 2% O_2, the CO emissions increase very rapidly which decreases boiler efficiency. Increasing the O_2 to 6.15% reduced the NO_x by nearly 9%, but with an accompanying decrease in efficiency.

Staged Combustion Air--

Staged combustion with natural gas fuel was evaluated with the gun burner in Test 185 and 186. Figure 3-13 shows the effect of secondary air injection depth on NO_x emissions. As was the case with the ring burner, the effect diminishes beyond 1.2 m (4 ft) injection depth with 85% of the reduction in the initial 1.2 m (4 ft). NO_x was reduced by approximately 38% by injecting the staged air at 1.2 m (4 ft) whereas at 2.1 m (7 ft), the NO_x was reduced by 46%. The burner equivalence ratio for these tests was 0.96.

Flue Gas Recirculation--

The effectiveness of flue gas recirculation as an NO_x reduction technique was evaluated with the boiler firing natural gas. Tests 172 through 177 were conducted with the flue gas recirculation rate varied up to a maximum rate of 20%. The initial gas burner configuration - a ring burner design - was unstable with even small amounts of recirculated flue gas. A narrow plate was installed in the burner to shield the gas jets from the flue gas but the combustion was still unstable. A gas gun burner was then installed and tested in place of the ring burner. A combination of gas orifices, swirl, gun and diffuser position was found which was stable with

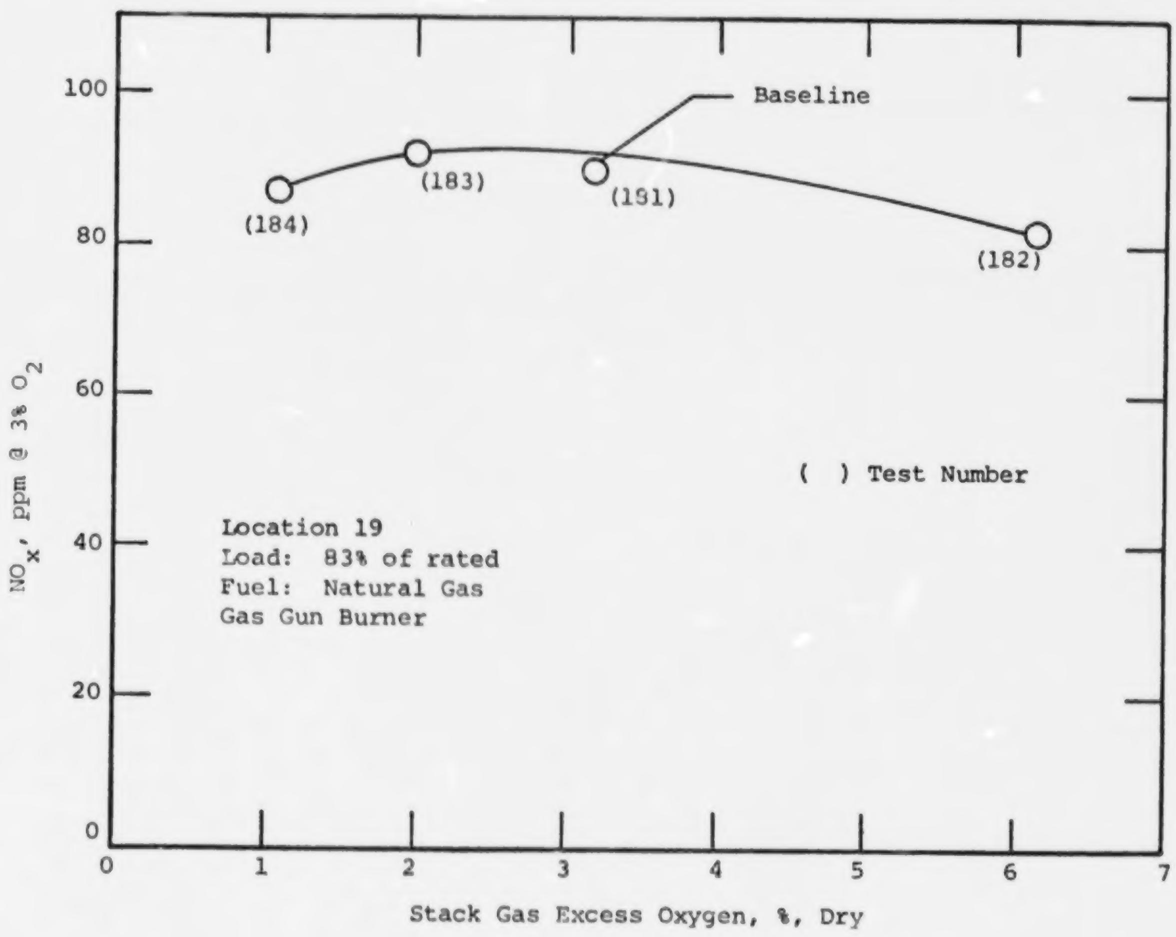


Figure 3-11. The effect of excess oxygen on NO_x emissions (natural gas; gas gun).

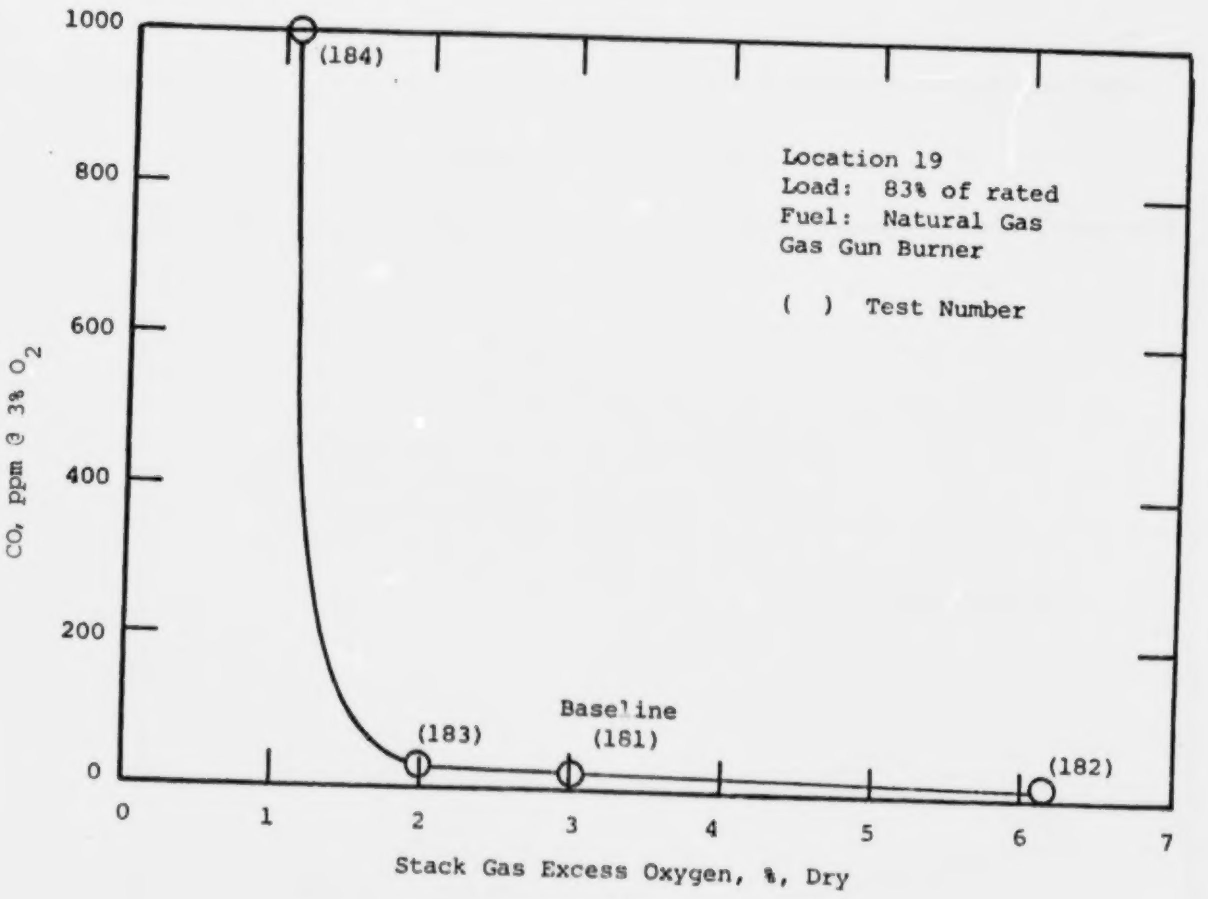


Figure 3-12. The effect of excess oxygen on CO emissions (natural gas; gas gun).

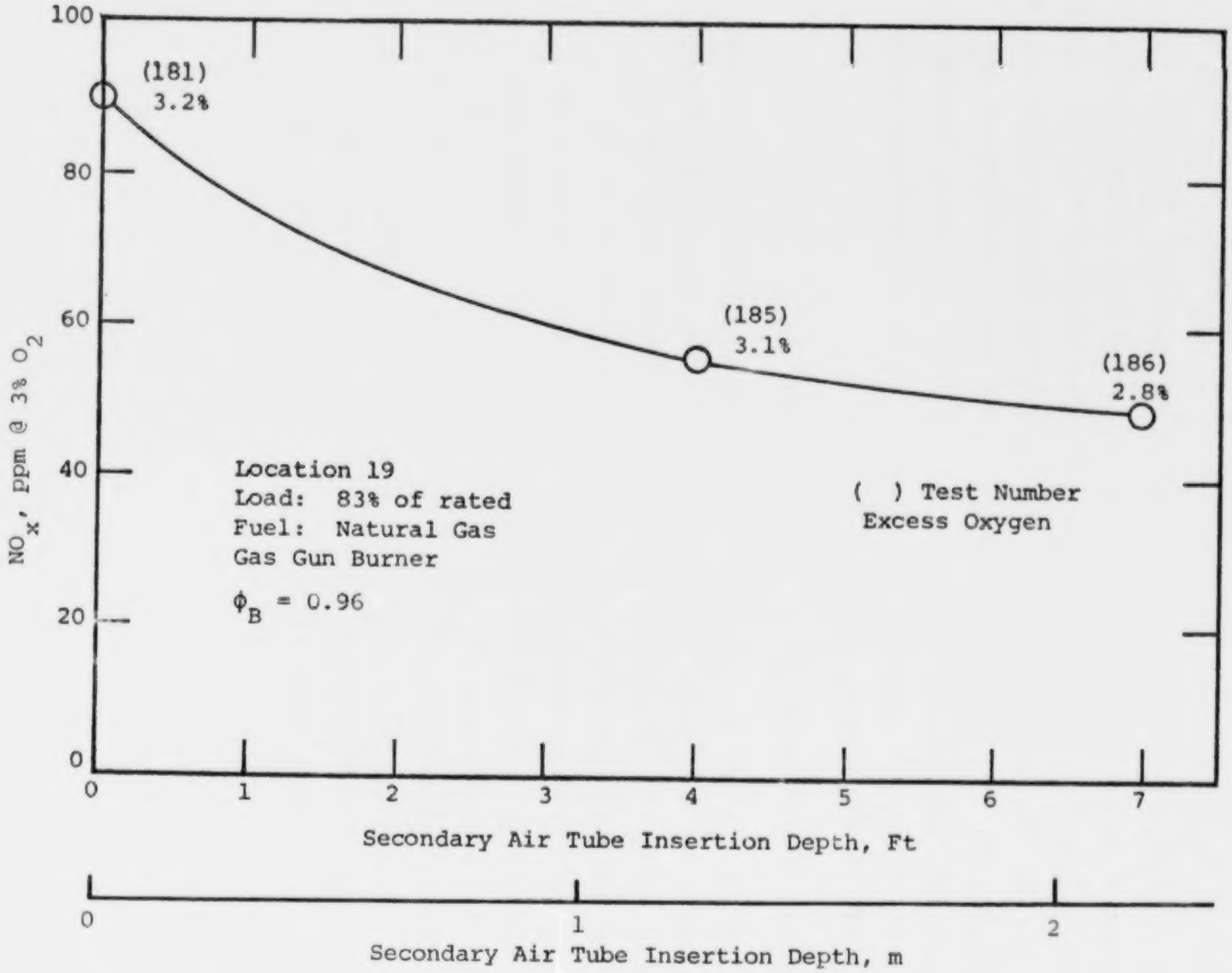


Figure 3-13. NO$_x$ emissions as a function of staged air injection depth (natural gas; gas burner).

high flue gas recirculation rates. The effect of flue gas recirculation on NO_x emissions is shown in Figure 3-14. The data indicate that even small amounts of flue gas recirculation (8%) result in relatively large (4[illegible]) reduction in NO_x emissions. At the maximum flue gas recirculation rate as limited by combustion stability, the reduction is 77% with the boiler operating at 3.2% O_2 and 79% with the boiler at 2.5% excess O_2.

Also illustrated in the figure is the effect of low O_2 operation in conjunction with flue gas recirculation. The amount of flue gas recirculated to the burner was increased until the flame stability limit was reached. With the gas gun burner, the maximum amount of flue gas which could be recirculated was approximately 20%. At the maximum recirculation rate, the measured NO_x value was 12.2 ng/J (24 ppm) at the normal O_2 condition. At low O_2 conditions, the measured NO_x value was 11.2 ng/J (22 ppm). These values represent reductions of 77% and 79% from the baseline condition.

Flue Gas Recirculation and Staged Combustion Air--

The effect of flue gas recirculation combined with staged combustion air was evaluated for the boiler firing natural gas with the gas gun burners. The tests were conducted with the maximum amount of staged combustion as limited by the secondary air flow. The staged air was injected at 1.2 m (4 ft) and 2.1 m (7 ft) for these tests. The percentage of recirculated flue gas was varied up to the maximum determined by burner stability limits. The maximum flue gas recirculation rate was 17.8%. The reduction in NO_x was 76% at the maximum recirculation rate of 17.8% and 68% at a recirculation rate of 11%. The combination of flue gas recirculation and staged combustion air gave the greatest reduction in NO_x, but only 5% more than flue gas recirculation alone. The effect of combined flue gas recirculation and staged combustion air is presented in Figure 3-15 for these tests.

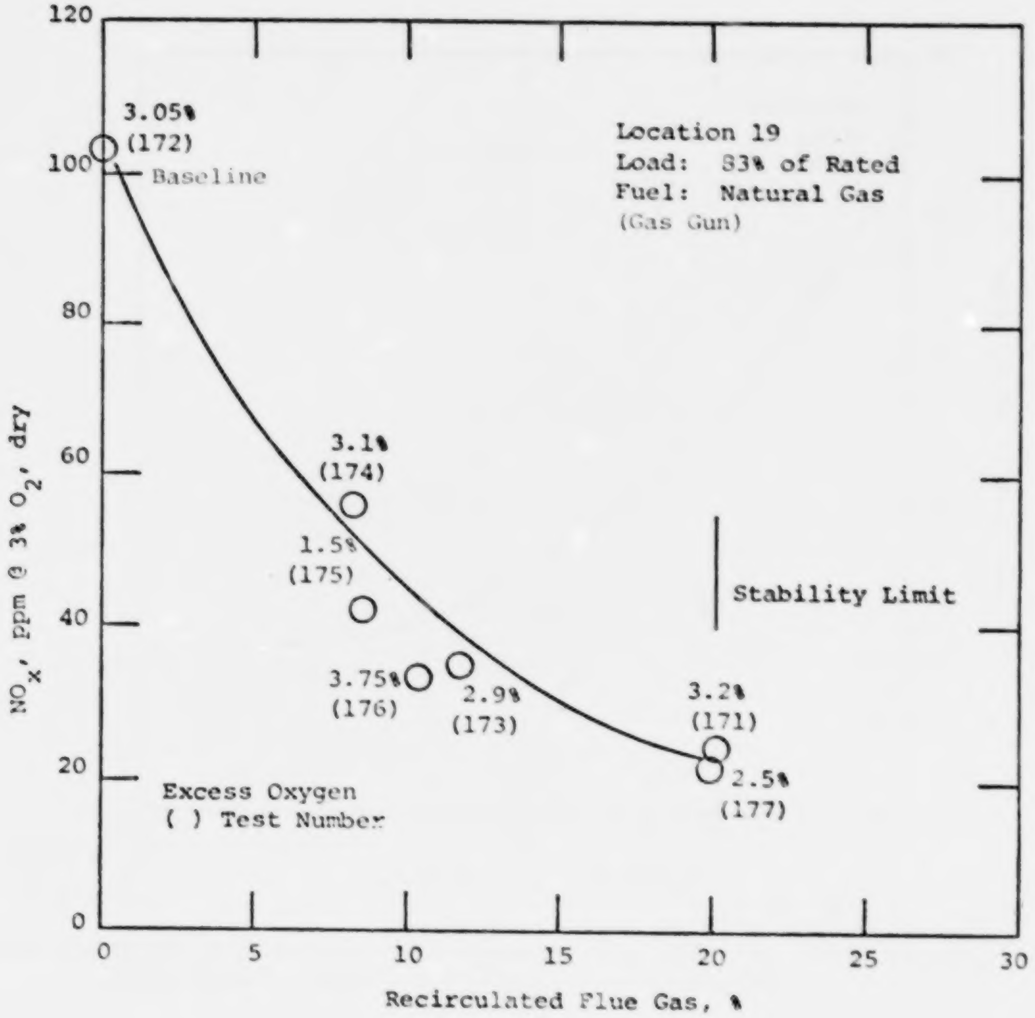


Figure 3-14. The effect of flue gas recirculation rate and low excess O_2 on NO_x emissions (natural gas).

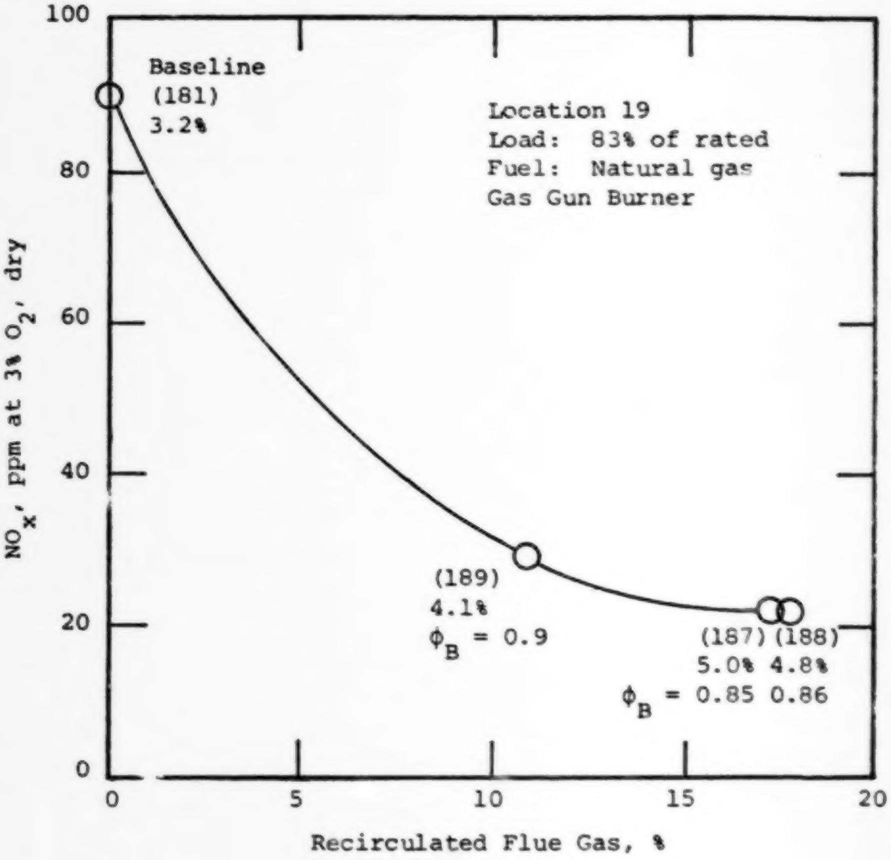


Figure 3-15. The effect of combined flue gas recirculation and staged combustion air on NO_x emissions (natural gas).

3.1.5 Particulate and SO_x Testing

Particulate tests were conducted at baseline conditions with the boiler firing #2 oil, #6 oil, and natural gas fuel. Particulate measurements were also made at low O_2 conditions, flue gas recirculation with low O_2, staged combustion air, and flue gas recirculation in combination with staged combustion air with #2 oil and #6 oil. A particulate test with flue gas recirculation and low O_2 was conducted on natural gas fuel. A summary of all Method 5 particulate measurements is presented in Table 3-4. With #2 oil, #6 oil, and natural gas all modified tests resulted in lower total particulate than measured at baseline conditions. Particulate size distributions are presented in Figure 3-16a for #6 oil and Figure 3-16b for #2 oil. These data show that for all but one test, between 30 and 50% of the particulate is 3 μm or less aerodynamic diameter.

Wet chemistry SO_x was measured firing #2 oil, #6 oil, and natural gas fuel at baseline and modified boiler conditions. Total sulfur oxides emissions for the boiler firing oil ranged from 68 ng/J (87 ppm) with #2 oil (0.13% S) to as high as 319 ng/J (409 ppm) with #6 oil (0.5 to 1.2% S). The level of sulfur oxides emissions is dependent solely upon the sulfur content of the fuel. A sulfur content of 1% in an oil fuel results in approximately 445 ng/J (580 ppm at 3% O_2) of sulfur oxides emissions. Total sulfur oxides emissions with natural gas were below detection for all tests except one, for which SO_x emissions were 18 ng/J (25 ppm) by the Dupont analyzer and 33 ng/J (47 ppm) by wet chemistry. SO_x varied from 10 to 30 ppm that test period (March 7-8, 1977). Because of the severe gas shortage (winter of '77) the natural gas may have not been of normal pipeline quality, which requires negligible sulfur.

3.1.6 Trace Species and Organics Emissions (TS&O)

Four tests were conducted at Location 19 to sample for trace species and organics. The sampling and analysis procedures are described in detail in Appendix A. Table 3-5 presents the sampling conditions for the trace species and organics tests. Two tests were conducted at baseline conditions (19-1,2) and two were at the optimum low-NO_x condition (19-3,4). All tests were conducted with #6 oil. After the initial baseline test, however, a new load of #6 oil was received by the operator. The new shipment of oil had

TABLE 3-4. SUMMARY OF METHOD 5 PARTICULATE MEASUREMENTS FOR LOCATION 19 STEAM BOILER

Boiler Operating Mode	No. 2 Oil		No. 6 Oil		Natural Gas	
	Total ng/J (lb/MMBtu)	Solid ng/J (lb/MMBtu)	Total ng/J (lb/MMBtu)	Solid ng/J (lb/MMBtu)	Total ng/J (lb/MMBtu)	Solid ng/J (lb/MMBtu)
Baseline	24.24 (0.0564)	2.595 (0.0060)	36.21 (0.084)	27.55 (0.064)	3.68 (0.0086)	1.92 (0.0045)
Low O_2	16.29 (0.0379)	5.95 (0.0138)	28.87 (0.0672)	25.80 (0.060)		
SCA	11.6 (0.0270)	9.01 (0.0210)	31.8 (0.0743)	27.2 (0.0635)		
FGR, Low O_2	5.84 (0.0136)	1.95 (0.0045)	32.33 (0.075)	29.36 (0.068)	2.63 (0.0061)	1.67 (0.0039)
FGR + SCA	4.16 (0.0097)	3.31 (0.0077)	28.80 (0.0670)	9.10 (0.021)		

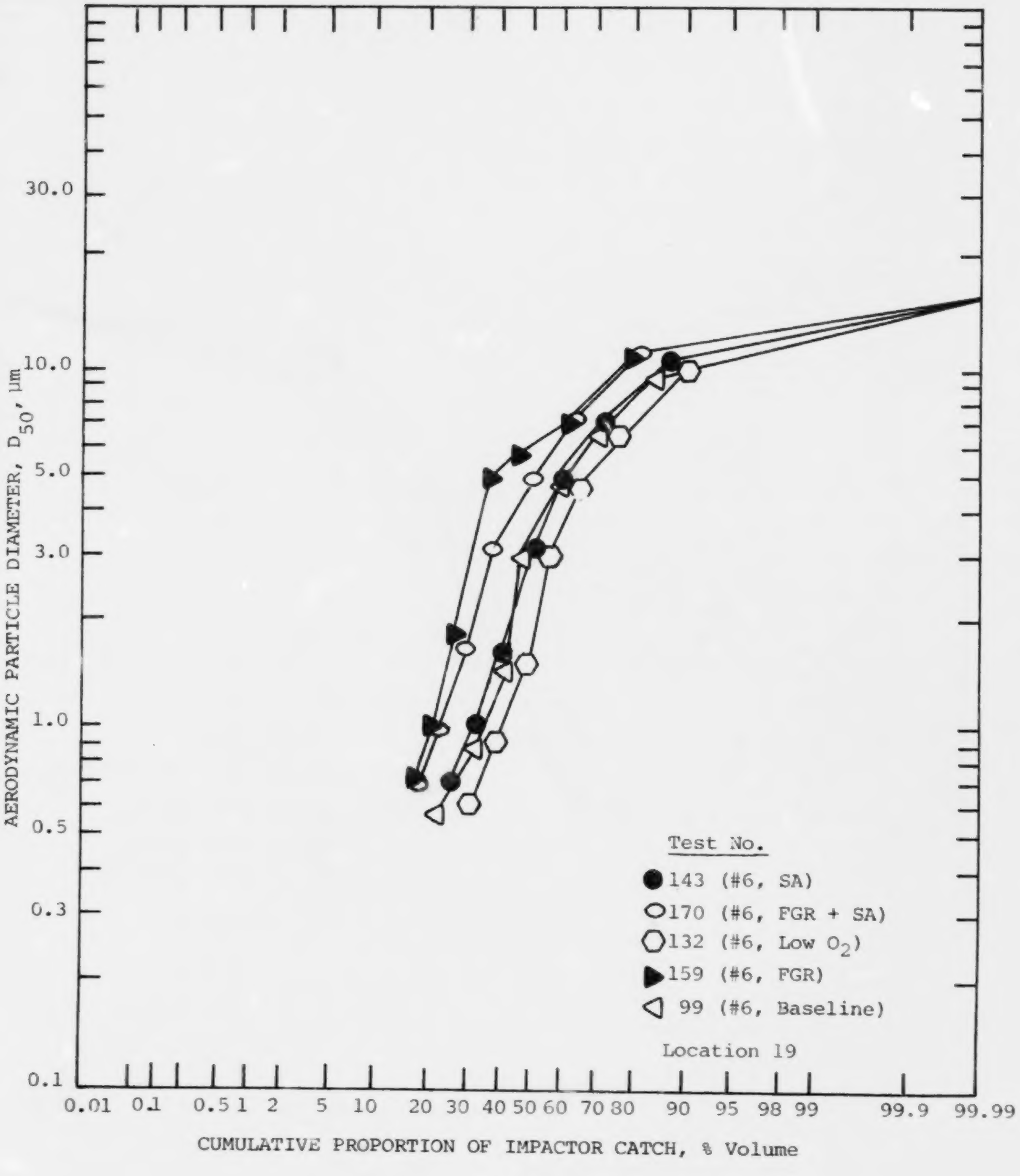


Figure 3-16a. Particulate size distribution for an oil fired steam boiler (No. 6 oil).

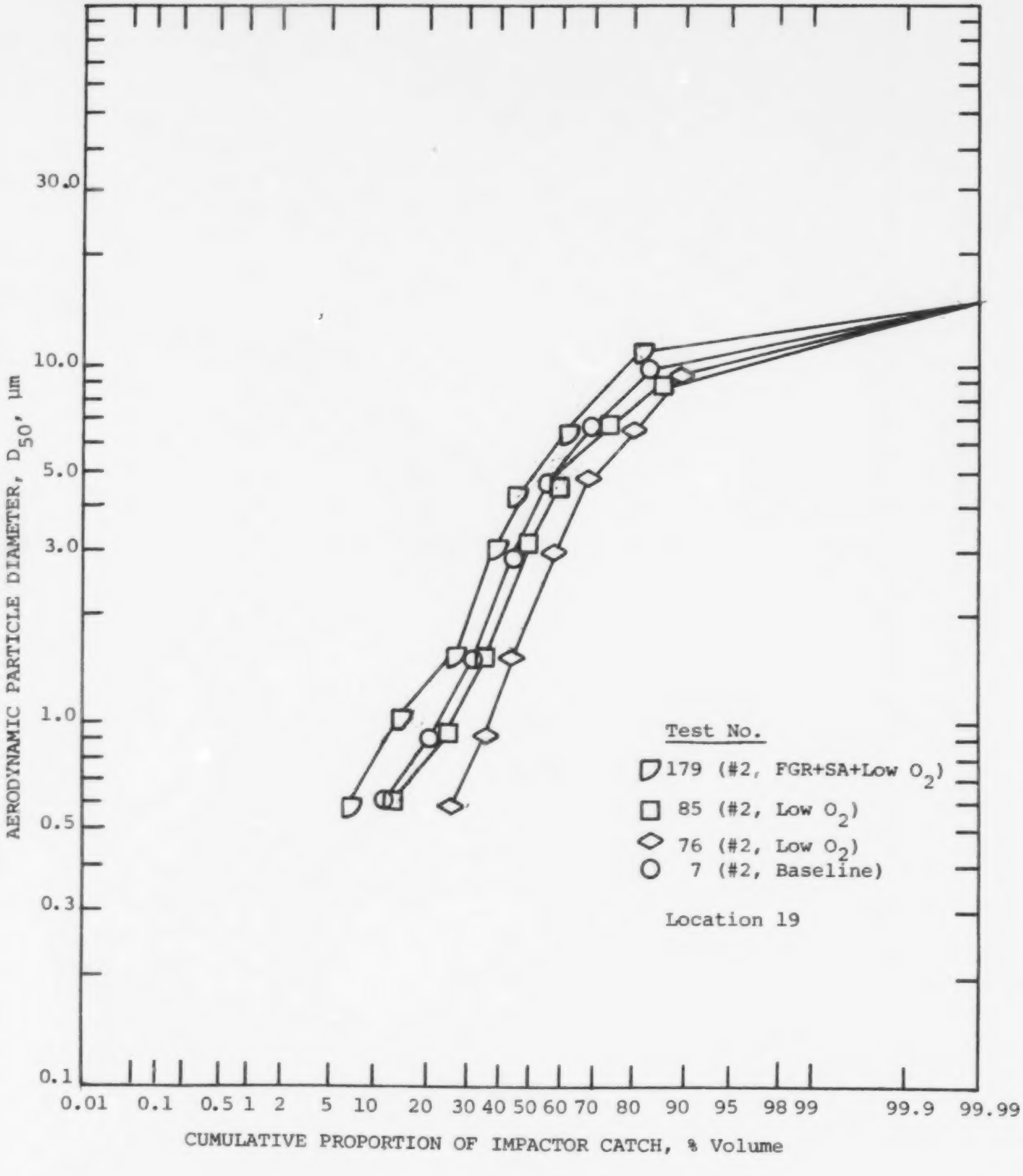


Figure 3-16b. Particulate size distribution for an oil fired steam boiler (No. 2 oil).

TABLE 3-5. TRACE SPECIES AND ORGANICS SAMPLING CONDITIONS, WATER TUBE BOILER - LOCATION 19

Test Number	19-1 SASS	19-2 SASS	19-3 SASS	19-4 SASS
Date	3/10/77	3/17/77	3/21/77	3/23/77
Port Location	stack	stack	stack	stack
Velocity, m/s (f/s)	7.55 (24.8)	7.23 (23.7)	7.37 (24.2)	6.95 (22.8)
Stack Temp., K (° F)	539 (511)	541 (514)	564 (556)	552 (534)
Oxygen Content, % Dry	2.9	3.0	1.8	1.5
Moisture, %	7.6	8.2	8.4	8.0
Sample Time, min.	300	300	300	300
Cyclone Flow, awm^3/m (awcfm)	0.115 (4.07)	0.118 (4.15)	0.120 (4.24)	0.117 (4.15)
Isokinetic Rate, %	99.7	107.4	110.9	114.7
Oven Temp., K (° F)	479 (402)	479 (402)	480 (405)	478 (400)
XAD-2 Temp., K (° F)	290 (63)	291 (64)	290 (62)	288 (59)
Nozzle Size, mm (in.)	19 (0.75)	19 (0.75)	19 (0.75)	19 (0.75)
No. of Filters Used	1	1	1	1
Sample Flow, Dry, DNm^3/m (scfm)	0.065 (2.31)	0.066 (2.35)	0.67 (2.38)	0.066 (2.35)
Volume Collected, Dry, DNm^3 (scf)	19.6 (693.6)	20.0 (704.7)	20.2 (713.3)	19.97 (705.8)
Particulate Collected, g	0.4289	2.7416	4.6981	3.8446
Solid Particulates, ng/J (lb/MMBtu)	6.26 (0.0146)	39.5 (0.092)	63.1 (0.147)	51.28 (0.119)
Unit Conditions				
Test Time, min.	305	302	302	302
Steam Flow, Mg/h (Mlb/h)	6.45 (14.3)	6.62 (14.6)	6.53 (14.4)	6.42 (14.1)
Fuel	#6 oil	#6 oil*	#6 oil*	#6 oil*

*New shipment of #6 oil received

significantly higher sulfur content than the original oil. Samples were taken and were submitted for analysis. All tests were conducted for five hours sample time. The samples were prepared by KVB and transmitted to the laboratory for analysis. Because of the significant difference in the fuel on Test 19-1, only SASS train samples from Tests 19-2, 3 and 4 were analyzed.

Table 3-6 presents the gaseous and particulate (by SASS) measurements and efficiency data. Table 3-7 presents the fuel sample analyses. The fuel analyses for Tests 19-2, 3 and 4 indicate sulfur content was twice that of the fuel for Test 19-1 and fuel nitrogen content was about 40% higher. Table 3-6 indicates that NO_x emissions increased by 15% for Test 19-2 compared with Test 19-1. This indicates that the fuel nitrogen conversion to NO_x was about 24%. Assuming 24% fuel nitrogen conversion for each test and subtracting the fuel nitrogen NO_x from total measured NO_x results in 77 ng/J (139 ppm) of thermal NO_x for both Test 19-1 and Test 19-2.

Tests 19-3 and 19-4 are duplicate runs at the optimum low NO_x condition with reduced excess air and maximum flue gas recirculation. NO_x emissions were reduced by 28% compared with the Test 19-2 baseline.

Total particulate emissions were significantly higher for Test 19-2 with the higher sulfur fuel compared with Test 19-1. There was a further increase in particulates of 30 to 60% for the two low NO_x tests compared with baseline Test 19-2 on the same fuel. These results are in contrast to previous results presented in Section 3.1.5 for which the comparable low NO_x condition produced no change in solid particulates as compared with baseline.

Samples were analyzed by atomic absorption (AA) and spark source mass spectrometry (SSMS) to determine concentrations of elements. Wet chemistry (WC) was used for chloride, fluoride, nitrate and sulfate. POM and PCB were analyzed by gas chromatography (GC). The XAD-2 resins for two tests (19-2, 19-3) were analyzed by gas chromatography-mass spectrometry (GC-MS) to quantify specific POM compounds. Appendix A contains the details of the analytical procedures.

TABLE 3-6. SUMMARY OF EMISSIONS DATA AT LOCATION 19 DURING TRACE SPECIES AND ORGANICS TESTS (TS&O)

Test Run	Date 1977	Steam Load Mg/h	Fuel	O_2 %	CO_2 %	NO_x* ng/J (ppm)	NO* ng/J (ppm)	HC* ng/J (ppm)	CO* ng/J (ppm)	SO_2* ng/J (ppm)	SASS Solid Partic. ng/J (lb/MMB)	Stack Temp. K (°F)	Eff. %	Smoke Spot	% FGR	Opacity	ϕ_B	Lance Depth m (ft)	Comments
19-1 SASS	3-10	5.51	#6	2.9	13.9	118 (213)	118 (213)	0.2 (1)	7 (20)	305 (395)	6.26 (0.0146)	541 (513)	82	0	0	0	--	--	Baseline TS&O Test
19-2 SASS	3-17	6.63	#6	3.0	13.8	135 (244)	135 (244)	1.3 (7)	12 (37)	638 (831)	39.5 (0.092)	543 (517)	82	0.5	0	2.5	--	--	Baseline TS&O Test New oil delivery
19-3 SASS	3-21	6.54	#6	1.8	14.5	97 (17[illegible])	97 (176)	0.6 (3)	55 (162)	627 (815)	63.1 (0.147)	562 (551)	81.8	1.0	34	7.5	--	--	Low O_2, Max. FGR TS&O Test
19-4 SASS	3-23	6.41	#6	1.5	14.4	98 (176)	98 (176)	-- --	37 (110)	578 (750)	51.28 (0.119)	560 (548)	82	0.5	35	5	--	--	Low O_2, Max. FGR TS&O Test

*Data reported on 3% O_2, dry basis

TABLE 3-7. SUMMARY OF LOCATION 19 TEST FUEL OIL ANALYSES FOR TRACE SPECIES AND ORGANICS TESTS

Fuel	#6 Oil	#6 Oil	#6 Oil	#6 Oil
Date	3-10-77	3-17-77	3-21-77	3-23-77
Test Number	19-1	19-2	19-3	19-4
Carbon, %	87.23	86.06	86.25	86.55
Hydrogen, %	11.34	11.11	11.25	11.26
Nitrogen, %	0.23	0.32	0.32	0.30
Sulfur, %	0.55	1.17	1.18	1.02
Ash, %	0.027	0.025	0.024	0.025
Oxygen, %	0.62	1.32	0.98	0.85
API Gravity	17.5	14.3	15.7	15.8
Heat Content kJ/kg	43845	43426	43589	43613
(Btu/lb)	(18850)	(18670)	(18740)	(18750)

Results of the trace species and organics analyses are presented in Tables 3-8 through 3-19. The following list provides a key to these tabulations:

Test	Table	Results
All	3-8	General Notes for all Tables
19-2	3-9	AA* for solids section
	3-10	AA for organic module and impingers
	3-11	AA for total emissions, fuel and mass balance
	3-12	SSMS* results (3 pages)
19-3	3-13	AA for solids section
	3-14	AA for organic module and impingers
	3-15	AA for total emissions, fuel and mass balance
	3-16	SSMS results (3 pages)
19-4	3-17	AA for solids section
	3-18	AA for organic module and impinger
	3-19	AA for total emissions, fuel and mass balance

The results are presented for each sample as concentration in the sample (μg/g) and in the stack flue gas ($\mu g/m^3$). For mass balance comparison the total emission rate and fuel input are presented as a flow rate (μg/s). Emissions contained in particles less than 3 microns collected by the 1 μm cyclone and filter are also given in Tables 3-11, 3-15, and 3-19 for each test.

The SSMS results are presented on three pages for each of two tests (19-2, 19-3). The first page contains the results for all elements also determined by AA analysis. The second and third pages contain results for all other elements as determined by SSMS.

All twenty-two inorganic elements specifically sought to be identified were detected in the SASS samples. Several elements (antimony, beryllium, mercury, selenium, tellurium and tin) could not be detected by AA analysis.

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* AA = Atomic absorption
SSMS = Spark source mass spectrometry

TABLE 3-8. GENERAL NOTES FOR TRACE SPECIES AND ORGANICS DATA TABULATIONS

1. All sample data are rounded to two significant digits and corrected for blanks.

2. Single number indicates all sample concentrations were above detection limits.

3. Single number preceded by "<" indicates all samples were less than detection limits. Value shown is maximum amount that could be present if the sample actually contained an amount equal to the detection limit value.

4. For two numbers separated by "<", the number on the left of < indicates the detected amount, and the number on the right indicates the maximum amount including the detected amount plus the amount that could be present in samples reported as below detection, if those samples actually contained an amount equal to the detection limit value.

5. < DL, concentration below detection limits

   =B, sample value equals blank, net value assumed zero

   < B, sample value less than blank, net value assumed zero

   MC, major component, exceeds maximum measureable quantity (about 1000 μg/g for spark source mass spectrometry)

   NES, not enough sample for adequate analysis

   NR, not reported, results uncertain because of complex sample matrix composition

6. Species for which either the emission rate or input (or both) were below detection limits have mass balance values indicated as follows:

   < DL, both emission and input below detection limit

   > value, input value is below detection limit or emission value is above detection limit

   < value, emission value is less than detection limit.

TABLE 3-9. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION

Test 19-2, Modified Boiler, Location 19, Baseline Condition

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
Sample Number	566		716		720		538		19-2A	
Sample Weight/Vol.	1.6620 g		0.4443 g		0.2196 g		0.4157 g		1605 ml	
Units	µg/g	µg/m³	µg/g	µg/m³	µg/g	µg/m³	µg/g	µg/m³	µg/ml	µg/m³
Antimony	< 38	< 3.2	< 210	< 4.7	< 230	< 2.7	< 500	< 10	< 0.5	< 40
Arsenic	< 1.5	< 0.13	33	0.73	< 10	< 0.11	200	4.2	0.018	1.4
Barium	38	3.2	460	10	6000	66	800	17	< 0.1	< 8
Beryllium	< 0.8	< 0.065	< 4.2	< 0.093	< 5	< 0.055	< 10	< 0.2	< 0.005	< 0.4
Cadmium	0.8	0.065	< 4.2	< 0.093	< 5	< 0.055	< 10	< 0.2	0.005	0.4
Calcium	1900	160	1900	42	3500	38	4800	100	0.49	39
Chromium	72	6	140	3.1	310	3.4	240	5	0.09	7.2
Cobalt	120	10	310	6.7	940	10	1600	33	< 0.2	< 16
Copper	46	3.8	50	1.1	100	1.1	460	9.6	0.06	4.8
Iron	5400	450	7200	160	32000	350	21000	440	2.6	210
Lead	150	13	< 20	< 0.44	< 25	< 0.27	1000	21	0.14	11
Manganese	51	4.3	75	1.7	210	2.3	250	5.2	0.17	14
Mercury	< 0.03	< 0.0025	< 0.17	< 0.0038	< 0.2	< 0.0022	< 0.4	< 0.008	< 0.005	< 0.4
Nickel	1900	160	2200	49	9000	99	30000	620	0.77	62
Selenium	< 1.5	< 0.13	< 8	0.18	< 10	< 0.11	< 20	< 0.42	< 0.01	0.8
Tellurium	< 38	< 3.2	< 210	< 4.7	< 250	< 2.7	< 500	< 10	< 0.3	< 24
Tin	< 76	< 6.3	< 420	< 9.3	< 500	< 5.5	<1000	< 21	< 1	< 80
Titanium	< 460	< 38	<1200	< 27	2500	27	<3000	< 62	< 1	< 80
Vanadium	6300	520	10000	220	43000	470	89000	1800	2.5	200
Zinc	400	33	400	8.9	1300	14	4900	100	1.7	140
Chloride	279	23	NES	NES	NES	NES	11600	240	2.1	170
Fluoride	205	17	134	3	909	10	< 2	< 0.04	< 0.1	< 8
Nitrates	113	9.4	NES	NES	NES	NES	39.5	0.82	0.24	19
Sulfates	14200	1200	NES	NES	NES	NES	457000	9500	7.0	560
Total POM	NES	NES	NES	NES	NES	NES	NES	NES	NR	NR
Total PCB	NES	NES	NES	NES	NES	NES	NES	NES	NR	NR

See notes on Table 3-8.

TABLE 3-10. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION

Test 19-2, Modified Boiler, Location 19, Baseline Condition

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1 Combined With Condensate		Impinger No. 2 Combined With Condensate		Impinger No. 3 Combined With Condensate	
Sample Number	533		19-2B		19-2C							
Sample Weight/Vol.	150 g		460 ml		4702 ml							
Units	$\mu g/g$	$\mu g/m^3$	$\mu g/ml$	$\mu g/m^3$	$\mu g/ml$	$\mu g/m^3$	$\mu g/ml$	$\mu g/m^3$	$\mu g/ml$	$\mu g/m^3$	$\mu g/ml$	$\mu g/m^3$
Antimony	< 25	< 190	< 0.5	< 12	< 0.5	< 120						
Arsenic	< 1	< 7.5	< 0.005	< 0.12	< 0.005	< 1.2						
Barium	< 50	< 75	< 0.1	< 2.3	< 0.1	< 24						
Beryllium	< 0.5	< 3.8	< 0.005	< 0.12	< 0.005	< 1.2						
Cadmium	< 1	< 7.5	0.34	7.8	0.018	4.2						
Calcium	40 - 10	230	0.16	3.7	0.028	6.6						
Chromium	5.8	44	14	320	1.4	330						
Cobalt	0	0	0.3	6.9	< 0.2	< 47						
Copper	0	0	0.14	3.2	0.036	8.5						
Iron	8	60	69	1600	4.3	1000						
Lead	< 2	< 15	< 0.05	< 1.2	< 0.04	< 9.4						
Manganese	1.5	11	0.70	16	0.074	17						
Mercury	< 0.02	< 0.15	< 0.005	< 0.12	< 0.005	< 1.2						
Nickel	< 2	< 15	8.9	200	0.7	160						
Selenium	< 1	< 7.5	< 0.01	< 0.23	< 0.01	< 2.4						
Tellurium	< 25	< 190	< 0.3	< 6.9	< 0.3	< 71						
Tin	< 50	< 380	< 1	< 23	< 1	< 230						
Titanium	< 150	< 1100	< 1	< 23	< 1	< 230						
Vanadium	< 1.5	< 75	0.2	4.6	< 0.1	< 23						
Zinc	8.4	63	0.03	0.7	0.04	9.4						
Chloride	0	0	< 0.5	< 12	49	12000						
Fluoride	0	0	0.16	3.7	0.57	130						
Nitrates	3.6	27	0.84	19	0.21	49						
Sulfates	67	500	260	6000	9800(SO_2)	2.3E6(SO_2)						
Total POM	0.005	0.04	NES	NES	< 0.001	< 0.24						
Total PCB	< 1	< 7.5	NES	NES	< 0.001	< 0.24						

See notes on Table 3-8.

TABLE 3-11. TRACE SPECIES AND ORGANIC EMISSIONS, PROCESS SAMPLES AND MASS BALANCES

Test 19-2, Modified Boiler, Location 19, Baseline Condition

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Input No. 6 Fuel Oil		Mass Balance
Sample Number	720,539	SASS		19-2LF		Emission / Input
Sample Weight/Vol.	0.6353 g	20 m^3	1.6 m^3/s	129 g/s		
Units	$\mu g/m^3$	$\mu g/m^3$	µg/s	µg/g	µg/s	
Antimony	< 13	< 380	< 610	< 25	< 3200	< DL
Arsenic	4	6.5 < 15	10 < 24	< 2	< 260	> 0.04
Barium	83	95 < 210	150 < 340	< 5	< 640	> 0.2
Beryllium	< 0.26	< 6	< 9.6	< 0.3	< 39	< DL
Cadmium	< 0.26	13	21	< 0.3	< 39	> 0.5
Calcium	140	650	1000	31	4000	0.25
Chromium	8.4	750	1200	< 5	< 640	> 1.9
Cobalt	43	65 < 130	100 < 210	< 10	< 1300	> 0.07
Copper	11	32	51	< 3	< 390	> 0.13
Iron	790	4300	6900	12	1500	4.6
Lead	21	45 < 70	70 < 110	< 3	< 390	> 0.18
Manganese	7.5	70	110	1.4	180	0.61
Mercury	< 0.01	< 1.9	< 3.0	< 0.1	< 13	< DL
Nickel	720	1300 < 1400	2100 < 2200	14	1800	1.2
Selenium	< 0.53	< 12	< 19	< 1	< 130	< DL
Tellurium	10 < 13	< 300	< 480	< 25	< 3200	< DL
Tin	< 26	< 750	< 1200	< 25	< 3200	< DL
Titanium	27 < 62	70 < 1600	110 < 2600	< 250	< 32000	> 0.003
Vanadium	2300	3200 < 3400	5200 < 5400	40	5200	1.0
Zinc	110	370	590	3	390	1.5
Chloride	240	12000	19000	< 11.6	< 1500	> 12
Fluoride	10	170 < 180	270 < 290	45.8	5900	0.05
Nitrates	0.8	130	210	NR	--	--
Sulfates	9500	18000	29000	NR	--	--
Total POM	NES	NES	NES	NR	--	--
Total PCB	NES	NES	NES	NR	--	--

See notes on Table 3-8.

TABLE 3-12. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY

Test 19-2, Modified Boiler, Location 19, Baseline Condition

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance	Best Balance AA & SS
Sample Number	19-2D		533		19-2F		SASS		19-2LF		Emission / Input	AA or SS Emission / AA or SS Input
Sample Weight/Vol.	2.7416 g		150 g		5162 ml		$20\ m^3$	$1.6\ m^3/s$	129 g/s			
Units	μg/g	$\mu g/m^3$	μg/g	$\mu g/m^3$	μg/ml	$\mu g/m^3$	$\mu g/m^3$	μg/s	μg/g	μg/s		
Antimony	26	3.6	1	7.5	< 0.001	0	11	18	< 0.15	< 20	> 0.90	--
Arsenic	18	2.5	0.4	3	0.004	1.0	6.5	10	0.3	39	0.26	0.26
Barium	MC	--	=B	0	=B	0	MC	MC	5	65	MC	2.30
Beryllium	0.4	0.055	< 0.4	< 3	< 0.001	< 0.26	0.055 < 3	0.09 < 5	< 0.15	< 20	> 0.005	--
Cadmium	0.6	0.08	< 0.7	< 5	0.03	7.5	7.5 < 13	12 < 21	< 0.15	< 20	> 0.60	> 1.05
Calcium	MC	--	30	220	7	1800	2000 < MC	3200 < MC	200	26000	0.12 < MC	0.80
Chromium	96	13	< B	0	3.7	950	960	1500	0.4	52	29	23.00
Cobalt	MC	--	< 0.1	< 0.8	0.027	7	8 < MC	13 < MC	2.5	320	0.04 < MC	0.31
Copper	280	38	=B	0	0.043	11	49	78	2	260	0.30	0.30
Iron	MC	--	4	30	5	1300	1300 < MC	2000 < MC	41	5100	0.39 < MC	1.35
Lead	380	52	< 2	< 15	=B	0	52 < 67	83 < 110	0.8	100	0.83 < 1.10	0.83
Manganese	140	19	0.1	0.8	0.19	49	69	110	0.3	39	2.82	0.61
Mercury	NR	--	NR	--	NR	--	NP	--	NR	--	--	--
Nickel	MC	--	< B	0	0.68	180	180 < MC	290 < MC	51	6600	0.04 < MC	1.20
Selenium	10	1.4	< 0.4	< 3	0.003	0.75	2 < 5	3 < 8	< 0.75	< 97	> 0.03	--
Tellurium	0.3	0.04	< 0.4	< 3	< 0.001	< 0.26	0.04 < 3	0.06 < 5	< 0.15	< 20	> 0.003	--
Tin	3	0.4	< 1	< 8	< B	0	0.4 < 8	0.6 < 13	< 0.45	< 58	> 0.01	--
Titanium	330	45	1.1	8	< B	0	53	85	0.9	120	0.71	0.92
Vanadium	MC	--	0.1	0.8	0.027	7	8 < MC	13 < MC	340	44000	MC	1.00
Zinc	MC	--	< B	0	< B	0	MC	MC	3.5	450	MC	1.30
Chlorine	32	4.3	< B	0	< B	0	4.3	6.9	2	260	0.027	--
Fluorine	59	8.1	2	15	< B	0	23	37	4	520	0.071	0.52

See notes on Table 3-8.

TABLE 3-12. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)

Test 19-2, Modified Boiler, Location 19, Baseline Condition

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance
Sample Number	19-2D		533		19-2F		SASS		19-2LF		Emission/Input
Sample Weight/Vol.	2.7416 g		150 g		5162 ml		$20\ m^3$	$1.6\ m^3/s$	129 g/s		
Units	μg/g	$\mu g/m^3$	μg/g	$\mu g/m^3$	μg/ml	$\mu g/m^3$	$\mu g/m^3$	μg/s	μg/g	μg/s	
Aluminum	MC	MC	3	23	< B	0	23 < MC	37 < MC	19	2500	--
Bismuth	0.3	0.04	< 0.4	< 3	< 0.001	0	0.04 < 3	0.06 < 5	< 0.1	< 13	> 0.005
Boron	18	2.5	=B	0	< B	0	2.5	4	0.6	77	0.05
Bromine	0.7	0.1	1	8	0.023	6	14	22	< 0.1	< 13	> 1.70
Cerium	0.1	0.01	< 0.6	< 5	< B	0	0.014 < 4.5	0.02 < 7	< 0.6	< 77	> 0.0003
Cesium	22	3	< 0.4	< 3	0.001	0.25	3.3	5.3	< 0.1	< 13	> 0.40
Dysprosium	1	0.14	< 0.4	< 3	< 0.001	< 0.3	0.14 < 3	0.22 < 5	< 0.1	< 13	> 0.02
Erbium	0.5	0.07	< 0.4	< 3	< 0.001	< 0.3	0.07 < 3	< 5	< 0.1	< 13	< DL
Europium	0.3	0.04	< 0.4	< 3	< 0.001	< 0.3	0.04 < 3	< 5	< 0.1	< 13	< DL
Gadolinium	1	0.14	< 0.4	< 3	< 0.001	< 0.3	0.14 < 3	< 5	< 0.1	< 13	< DL
Gallium	12	1.6	< 0.3	< 2	< 0.001	< 0.3	1.7 < 4	2.7 < 6	< 0.1	< 13	> 0.20
Germanium	0.8	0.1	< 0.4	< 3	< 0.001	< 0.3	0.1 < 3	0.2 < 5	< 0.1	< 13	> 0.02
Gold	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Hafnium	0.5	0.07	< 0.4	< 3	< 0.001	< 0.3	0.07 < 3	0.1 < 5	< 0.1	< 13	> 0.01
Holmium	0.7	0.1	< 0.4	< 3	< 0.001	< 0.3	0.1 < 3	0.2 < 5	< 0.1	< 13	> 0.02
Iodine	0.4	0.05	0.5	4	0.0025	0.65	4.7	7.5	0.5	64	0.12
Iridium	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Lanthanum	190	26	< 0.4	< 3	< B	0	26	42	< 0.1	< 13	> 3.2
Lithium	4	0.5	< 0.4	< 3	< B	0	0.5 < 3	< 5	< 0.1	< 13	< DL
Lutetium	0.1	0.01	< 0.4	< 3	< 0.001	< 0.3	0.01 < 3	< 5	< 0.1	< 13	< DL
Magnesium	MC	MC	=B	0	< B	0	MC	MC	24.0	3000	--
Molybdenum	MC	MC	2	15	0.13	33	48 < MC	77 < MC	6.0	773	> 0.10
Neodymium	19	2.6	< 0.4	< 3	< 0.001	< 0.3	3 < 6	5 < 10	< 0.1	< 13	> 0.38
Niobium	0.4	0.05	< 0.4	< 3	< 0.001	< 0.3	0.05 < 3	0.08 < 5	< 0.1	< 13	> 0.006
Osmium	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL

See note on Table 3-8.

TABLE 3-12. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)

Test 19-2, Modified Boiler, Location 19, Baseline Condition

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance
Sample Number	19-2D		533		19-2F		SASS		19-2LF		Emission / Input
Sample Weight/Vol.	2.7416 g		150 g		5162 ml		$20\ m^3$	$1.6\ m^3/g$	129 g/s		
Units	µg/g	$\mu g/m^3$	µg/g	$\mu g/m^3$	µg/ml	$\mu g/m^3$	$\mu g/m^3$	µg/s	µg/g	µg/s	
Palladium	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Platinum	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Phosphorus	MC	MC	2	15	=B	0	15 < MC	24 < MC	29	3700	> 0.004
Potassium	MC	MC	2	15	1.9	480	495 < MC	800 < MC	23	3000	> 0.17
Praseodymium	11	1.5	< 0.4	< 3	< 0.001	< 0.3	1.5 < 3	2.4 < 5	< 0.1	< 13	> 0.9
Rhenium	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Rhodium	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Rubidium	1	0.15	=B	0	< B,DL	0	0.15	0.24	< 0.1	< 13	> 0.02
Ruthenium	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Samarium	2	0.3	< 0.4	< 3	< 0.001	< 0.3	0.3 < 3	0.5 < 5	< 0.1	< 13	> 0.03
Scandium	0.2	0.03	< 0.1	< 0.8	< 0.001	< 0.3	0.03 < 1	0.05 < 2	< 0.1	< 13	> 0.003
Silicon	MC	MC	15	110	0.58	150	260 < MC	420 < MC	23	3000	> 0.14
Silver	7	1.0	< 0.8	< 6	MC	-	1 < MC	2 < MC	0.1	< 13	> 0.15
Sodium	MC	MC	5	38	> 0.12	> 30	38 < MC	60 < MC	210	27000	> 0.002
Sulfur	MC	MC	93	690	MC	MC	690 < MC	1100 < MC	MC	MC	--
Strontium	110	15	=B	0	< B	0	15	24	1	130	0.18
Tantalum	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Thallium	< 0.1	< 0.014	< 0.4	< 3	< 0.001	< 0.3	< 3	< 5	< 0.1	< 13	< DL
Terbium	0.3	0.04	< 0.4	< 3	< 0.001	< 0.3	0.04 < 3	0.06 < 5	< 0.1	< 13	> 0.005
Thorium	1	0.15	< 0.4	< 3	< 0.006	< 1.6	0.15 < 4	0.24 < 6	< 0.1	< 13	> 0.02
Thulium	0.1	0.02	< 0.4	< 3	< 0.001	< 0.3	0.02 < 3	0.03 < 5	< 0.1	< 13	> 0.002
Tungsten	0.8	0.1	< 0.4	< 3	< 0.001	< 0.3	0.1 < 3	0.2 < 5	< 0.1	< 13	> 0.02
Uranium	< 0.7	< 0.1	< 0.4	< 3	< 0.004	< 1.0	< 4	< 6	< 0.1	< 13	< DL
Ytterbium	0.7	0.1	< 0.4	< 3	< 0.001	< 0.3	0.1 < 3	0.2 < 5	< 0.1	< 13	> 0.02
Yttrium	1	0.15	< 0.4	< 3	< 0.001	< 0.3	0.2 < 3	0.3 < 5	< 0.1	< 13	> 0.02
Zirconium	5	0.7	1	8	=B	0	9	14	0.9	120	0.12

See note on Table 3-8.

TABLE 3-13. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION

Test 19-3, Modified Boiler, Location 19, Low NO_x Condition

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
Sample Number	722		723		726		539		19-3A	
Sample Weight/Vol.	2.4163 g		1.0724 g		0.2120 g		0.9974 g		1839 ml	
Units	µg/g	µg/m³	µg/g	µg/m³	µg/g	µg/m³	µg/g	µg/m³	µg/ml	µg/m³
Antimony	< 50	< 6	< 2500	< 130	< 830	< 9	< 170	< 8	< 0.5	< 46
Arsenic	4	0.5	< 100	< 5	< 33	< 0.4	33	1.6	0.01	0.[illegible]
Barium	480	57	< 1000	< 53	< 330	< 4	730	36	< 0.1	< 9
Beryllium	< 1	< 0.12	< 50	< 3	< 17	< 0.2	< 3.3	< 0.2	< 0.005	< 0.5
Cadmium	< 1	< 0.12	< 50	< 3	< 17	< 0.2	< 3.3	< 0.2	< 0.005	< 0.5
Calcium	1900	230	3500	190	3000	31	3100	150	15	1400
Chromium	69	8	950	50	300	3.1	180	8.9	0	0
Cobalt	104	12	450	24	300	3.1	807	40	< 0.2	< 18
Copper	43	5	< 50	< 3	< 150	< 2	200	9.9	0.11	10
Iron	5200	620	4400	230	6500	68	20000	1000	1.8	160
Lead	NES	--	NES	--	NES	--	NES	--	0.11	10
Manganese	49	6	200	11	117	1.2	160	7.9	0.16	15
Mercury	0.5	0.06	< 2	< 0.1	< 0.67	< 0.007	< 0.13	< 0.006	< 0.005	< 0.5
Nickel	970	120	1700	90	3000	31	13000	640	0.5	46
Selenium	< 2	0.24	< 5000	< 270	< 33	< 0.4	< 6.7	< 0.3	0.04	3.6
Tellurium	< 50	6	< 2500	< 130	< 830	< 9	< 170	< 8	< 0.3	< 27
Tin	< 100	12	< 5000	< 270	<1700	< 18	< 330	< 16	< 1	< 91
Titanium	600	72	<15000	< 800	5000	52	<1000	< 49	< 1	< 91
Vanadium	5400	650	7000	370	14000	150	43000	2100	1.4	130
Zinc	281	34	250	13	350	3.7	3000	150	0.49	45
Chloride	< 30	< 4	< 97	< 5	NES	--	1700	84	< 0.5	< 46
Fluoride	54	6.5	NES	--	NES	--	< 1	< 0.05	< 0.1	< 9
Nitrates	43	5.1	67	3.6	NES	--	46	2.3	0.26	24
Sulfates	8910	1100	14000	740	NES	--	170000	8400	12	1100
Total POM	< 1	< 0.1	NES	--	NES	--	NES	--	NR	--
Total PCB	< 1	< 0.1	NES	--	NES	--	NES	--	NR	--

See notes on Table 3-8.

TABLE 3-14. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION

Test 19-3, Modified Boiler, Location 19, Low NO_x Condition

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1 Combined With Condensate		Impinger No. 2 Combined With Condensate		Impinger No. 3 Combined With Condensate	
Sample Number	537		19-3B		19-3C							
Sample Weight/Vol.	150 g		703 ml		4616 ml							
Units	μg/g	μg/m^3	μg/ml	μg/m^3	μg/ml	μg/m^3	μg/ml	μg/m^3	μg/ml	μg/m^3	μg/ml	μg/m^3
Antimony	< 25	< 186	< 0.5	< 17	< 0.50	< 110						
Arsenic	7	52	0.005	0.2	0.005	1.1						
Barium	75	560	< 0.1	< 3.5	< 0.1	< 23						
Beryllium	< 0.5	< 4	< 0.005	< 0.2	< 0.005	< 1						
Cadmium	< 0.5	< 4	0.015	0.52	0.018	4.1						
Calcium	< B	0	0.02	0.70	0							
Chromium	5.3	39	8.4	290	1.5	340						
Cobalt	< B	0	< 0.2	< 7	< 0.2	< 50						
Copper	< B	0	0.11	3.8	0.05	11						
Iron	11	82	38	1300	5.2	1200						
Lead	< B	0	< 0.05	< 2	< 0.04	< 9						
Manganese	1.5	11	0.57	20	0.12	27						
Mercury	< 0.02	< 0.2	< 0.005	< 0.2	< 0.005	< 1						
Nickel	< 2.5	< 19	5.9	200	2.0	460						
Selenium	< 1	< 8	0.04	1.4	0.02	4.6						
Tellurium	< 25	< 190	< 0.3	< 10	< 0.3	< 69						
Tin	< 50	< 370	< 1	< 35	< 1.0	< 230						
Titanium	< 150	<1100	< 1	< 35	< 1.0	< 230						
Vanadium	< 10	< 74	< 0.1	< 3.5	< 0.1	< 23						
Zinc	=B	0	=B	0	2.5	570						
Chloride	< B	0	1.6	56	15	3400						
Fluoride	< B	0	< 0.1	< 4	0.3	69						
Nitrates	0.2	1.5	0.88	31	0.22	50						
Sulfates	289	2100	130	4500	5400 (SO_2)	1.2×10^6 (SO_2)						
Total POM	0.0008	0.006	1.45	50	0.002	0.5						
Total PCB	< 1	< 7	< 0.001	< 0.03	< 0.001	< 0.2						

See notes on Table 3-8.

TABLE 3-15. TRACE SPECIES AND ORGANIC EMISSIONS, PROCESS SAMPLES AND MASS BALANCES

Test 19-3, Modified Boiler, Location 19, Low NO_x Condition

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	Input No. 6 Fuel Oil		Mass Balance
Sample Number	726,539	SASS		19-3LF		Emission/Input
Sample Weight/Vol.	1.2094 g	20.2 m^3	1.495 m^3/s	128.1 g/s		
Units	µg/m^3	µg/m^3	µg/s	µg/g	µg/s	
Antimony	< 17	< 540	< 810	< 25	< 3200	< DL
Arsenic	1.6 < 2	59 < 64	88 < 96	< 2	< 260	> 0.24
Barium	36 < 40	640 < 740	960 < 1100	< 5	< 640	> 1.50
Beryllium	< 0.34	< 8.9	< 13	< 0.3	< 38	< DL
Cadmium	< 0.34	4.8 < 12	7.2 < 18	< 0.3	< 38	> 0.19
Calcium	181	2000	3000	< 10	< 1300	> 2.30
Chromium	12	740	1100	< 5	< 640	> 1.70
Cobalt	43	79 < 150	120 < 220	< 10	< 1300	> 0.10
Copper	9.9 < 12	39 < 44	58 < 66	< 3	< 380	> 0.15
Iron	1000	4700	7000	7	900	7.8
Lead	NES	9.9 < 21	15 < 31	< 3	< 380	> 0.04
Manganese	9.1	99	150	< 0.5	< 64	> 2.30
Mercury	< 0.013	0.06 < 21	0.09 < 3.1	< 0.1	< 13	> 0.007
Nickel	670	1600	2400	< 10	< 1300	> 1.80
Selenium	< 0.65	9.9 < 290	15 < 430	< 1	< 130	> 0.12
Tellurium	< 17	< 450	< 670	< 25	< 3200	< DL
Tin	< 34	< 1000	< 1500	< 25	< 3200	< DL
Titanium	52 < 100	120 < 2500	180 < 3700	< 250	< 32000	> 0.006
Vanadium	2200	3400 < 3600	5100 < 5400	50	6400	0.80
Zinc	150	820	1200	5	640	1.90
Chloride	84	3500	5200	< 34.4	< 4400	> 1.20
Fluoride	< 0.05	64 < 79	96 < 120	< 34.6	< 4400	0.02
Nitrates	2.3	110 < 120	160 < 180	NR	--	--
Sulfates	8400	18000	27000	NR	--	--
Total POM	NES	50 < 51	75 < 76	NR	--	--
Total PCB	NES	< 7	< 11	NR	--	--

See notes on Table 3-8.

TABLE 3-16. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY

Test 19-3, Modified Boiler, Location 19, Low NO_x Condition

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance	Best Balance AA & SS
Sample Number	19-3D		537		19-3F		SASS		19-3LF		Emission / Input	AA or SS Emission / AA or SS Input
Sample Weight/Vol.	4.6981 g		150 g		5319 ml		20.2 m^3	1.5 m^3/s	128 g/s			
Units	µg/g	µg/m^3	µg/g	µg/m^3	µg/ml	µg/m^3	µg/m^3	µg/s	µg/g	µg/s		
Antimony	20	4.7	17	130	0.1	26	160	240	< 0.2	< 30	> 9.00	--
Arsenic	7	1.6	< 0.7	< 5	0.02	5	6 < 12	9 < 18	0.4	51	0.18 < 0.35	1.7
Barium	460	110	< B	< 0	2	530	640	960	4	510	1.90	1.90
Beryllium	0.1	0.02	< 0.2	< 2	0.001	0.26	0.3 < 2	0.5 < 3	< 0.2	< 30	> 0.02	--
Cadmium	0.4	0.09	< 0.3	< 2	< 0.01	< 3	0.09 < 5	0.1 < 8	< 0.2	< 30	> 0.004	--
Calcium	MC	MC	9	67	MC	MC	67 < MC	100 < MC	43	5500	MC	0.55
Chromium	33	7.7	3	22	1.8	470	500	750	2	260	2.90	2.90
Cobalt	400	93	< 0.1	< 0.7	=B	0	94	140	2	260	0.54	0.54
Copper	70	16	2	15	0.4	100	130	190	1.5	190	1.00	1.00
Iron	MC	MC	8	59	4	1000	1100	1600	14	1800	0.89	0.89
Lead	160	37	1	7	0.04	10	54	81	< 0.9	< 110	> 0.74	--
Manganese	44	10	0.2	1.5	0.2	50	64	96	0.45	58	1.66	1.66
Mercury	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	--
Nickel	MC	MC	1	7	0.8	210	240 < MC	360 < MC	23	2900	MC	0.83
Selenium	3	0.7	< 0.4	< 3	0.4	100	100 < 110	150 < 160	0.9	110	1.40	1.40
Tellurium	0.8	0.2	< 0.2	< 2	< 0.006	< 2	0.2 < 3	0.3 < 5	< 0.2	< 30	> 0.01	--
Tin	5	1.2	0.4	3	0.03	8	12	18	< 0.2	< 30	> 0.70	--
Titanium	300	70	1.1	8	1.9	500	580	870	1	130	6.70	1.40
Vanadium	MC	MC	0.5	4	0.02	5	9 < MC	13 < MC	150	19000	MC	0.80
Zinc	570	130	6	45	1.9	500	680	1000	2.5	320	3.10	1.60
Chlorine	160	37	14	100	7.7	2000	2100	3200	1.5	190	17.00	17.00
Fluorine	46	11	22	160	=B	0	170	260	3	380	0.70	0.70

See notes on Table 3-8.

TABLE 3-16. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)

Test 19-3, Modified Boiler, Location 19, Low NO_x Condition

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance
Sample Number	19-3D		537		19-3F		SASS		19-3LF		Emission / Input
Sample Weight/Vol.	4.6981 g		150 g		5319 ml		$20.2 m^3$	$1.50 m^3/s$	128 g/s		
Units	µg/g	µg/m^3	µg/g	µg/m^3	µg/ml	µg/m^3	µg/m^3	µg/s	µg/g	µg/s	
Aluminum	> 130	> 30	=B	0	> 7	> 1800	> 1800	> 2700	2	260	> 10.00
Bismuth	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Boron	1	0.23	=B	0	< B	0	0.23	0.35	0.7	90	0.004
Bromine	2	0.46	=B	0	0.28	74	74	110	< 0.5	< 60	> 1.80
Cerium	19	4.4	0.2	1.5	0.007	1.8	7.7	12	< 0.2	< 30	> 0.40
Cesium	0.8	0.19	< 0.1	< 0.7	0.03	8	8.2 < 9	12 < 14	< 0.2	< 30	> 0.40
Dysprosium	0.8	0.19	< 0.2	< 2	< 0.006	< 2	0.2 < 4	0.3 < 6	< 0.2	< 30	> 0.01
Erbium	0.2	0.05	< 0.2	< 2	< 0.006	< 2	0.05 < 4	0.07 < 6	< 0.2	< 30	> 0.002
Europium	0.3	0.07	< 0.2	< 2	< 0.006	< 2	0.07 < 4	0.11 < 6	< 0.2	< 30	> 0.004
Gadolinium	0.7	0.16	< 0.2	< 2	< 0.006	< 2	0.16 < 4	0.24 < 6	< 0.2	< 30	> 0.01
Gallium	11	2.6	< 0.1	< 0.7	< 0.006	< 2	2.6 < 5	3.9 < 8	< 0.2	< 30	> 0.13
Germanium	0.6	0.14	< 0.2	< 1.5	< 0.006	< 2	0.14 < 4	0.21 < 6	< 0.2	< 30	> 0.01
Gold	< 0.1	< 0.02	1	7.4	< 0.02	< 5	7.4 < 9	11 < 14	< 0.2	< 30	> 0.40
Hafnium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Holmium	0.4	0.09	< 0.2	< 2	< 0.006	< 2	0.09 < 4	0.13 < 6	< 0.2	< 30	> 0.004
Iodine	1	0.23	0.3	2.2	0.02	5	7.4	11	< 0.2	< 30	> 0.40
Iridium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Lanthanum	60	14	0.4	3	0.024	6	23	35	< 0.2	< 30	> 1.20
Lithium	2	0.46	< 0.1	< 0.7	0.034	9	9.5 < 10	14 < 15	< 0.1	< 13	> 1.08
Lutotium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Magnesium	MC	MC	10	74	MC	MC	74 < MC	110 < MC	27	3400	> 0.03
Molybdenum	970	230	9	67	0.24	63	360	540	8	1000	0.54
Neodymium	12	2.8	< 0.2	< 2	< 0.006	< 2	2.8 < 6	< 9	< 0.2	< 30	< DL
Niobium	0.7	0.16	< 0.2	< 2	< 0.02	5	5.2 < 7	< 11	< 0.4	< 50	< DL
Osmium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL

See note on Table 3-8.

TABLE 3-16. TRACE SPECIES EMISSIONS BY SPARK SOURCE MASS SPECTROMETRY (Continued)

Test 19-3, Modified Boiler, Location 19, Low NO_x Condition

Sample Type	Combined Solids		XAD-2 Resin		Combined Liquids		Total Emission Concen.	Total Emission Rate	Input No. 6 Fuel Oil		SSMS Mass Balance
Sample Number	19-3D		537		19-3F		SASS		19-3LF		Emission/Input
Sample Weight/Vol.	4.6981 g		150 g		5319 ml		20.2 m^3	1.50 m^3/s	128 g/s		
Units	µg/g	µg/m^3	µg/g	µg/m^3	µg/ml	µg/m^3	µg/m^3	µg/s	µg/g	µg/s	
Palladium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	30	< DL
Platinum	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Phosphorus	MC	MC	11	82	MC	MC	82 < MC	120 < MC	11	1400	> 0.09
Potassium	MC	MC	=B	0	MC	MC	MC	MC	8	1000	--
Praseodymium	7	2	< 0.2	< 2	< 0.006	< 2	2 < 6	3 < 8	< 0.2	< 30	> 0.10
Rhenium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Rhodium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Rubidium	0.8	0.2	< B	0	0.002	0.5	0.7	4	< 0.1	< 13	> 0.31
Ruthenium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Samarium	2	0.5	< 0.2	< 2	< 0.006	< 2	0.5 < 5	0.8 < 8	< 0.2	< 30	--
Scandium	0.2	0.05	< 0.1	0.7	< 0.009	2.4	3	5	< 0.2	< 30	> 0.17
Silicon	MC	MC	15	110	2.6	690	800 < MC	1200 < MC	19	2400	> 0.50
Silver	5	1.2	0.7	5	MC	MC	6 < MC	9 < MC	2	260	> 0.03
Sodium	> 330	> 77	39	290	MC	MC	360 < MC	550 < MC	72	9200	> 0.06
Sulfur	> 800	>190	21	160	MC	MC	350 < MC	530 < MC	MC	MC	--
Strontium	42	9.8	< B	0	1	260	270	410	1	130	3.10
Tantalum	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Thallium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Terbium	0.2	0.05	< 0.2	< 2	< 0.006	< 2	0.05 < 4	0.8 < 6	< 0.2	< 30	> 0.03
Thorium	< 1	< 2	< 1	< 7	< 0.06	< 20	< 29	< 44	< 0.2	< 30	< DL
Thulium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Tungsten	< 0.7	< 0.2	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Uranium	2	0.5	< 1	< 7	0.1	26	27 < 33	41 < 50	< 0.2	< 30	> 1.40
Ytterbium	< 0.1	< 0.02	< 0.2	< 2	< 0.006	< 2	< 4	< 6	< 0.2	< 30	< DL
Yttrium	2	0.5	< 0.2	< 2	< 0.008	< 2	0.5 < 4	0.8 < 6	< 0.2	< 30	> 0.03
Zirconium	7	2	< B	0	0.02	6	8	12	0.6	77	0.15

See note on Table 3-8.

TABLE 3-17. TRACE SPECIES AND ORGANIC EMISSIONS, SASS SOLIDS SECTION COLLECTION

Test 19-4, Modified Boiler, Location 19, Low NO$_x$ Condition

Sample Type	Nozzle, Probe, 10 µm Cyclone Solids		3 µm Cyclone Solids		1 µm Cyclone Solids		Filters		Solid Section Wash	
Sample Number	728		732		734		540		19-4A	
Sample Weight/Vol.	1.5802 g		0.9878 g		0.3263 g		0.9503 g		1760 ml	
Units	µg/g	µg/m^3	µg/g	µg/m^3	µg/g	µg/m^3	µg/g	µg/m^3	µg/ml	µg/m^3
Antimony	< 50	< 4	< 100	< 5	< 125	< 2	< 100	< 5	< 0.5	< 44
Arsenic	20	1.6	20	1	50	0.8	46	2.2	0.005	0.4
Barium	140	11	2400	120	625	10	650	31	< 0.1	< 9
Beryllium	< 1	< 0.08	< 2	< 0.1	< 2.5	< 0.04	< 2	< 0.1	< 0.005	< 0.4
Cadmium	< 1	< 0.08	< 2	< 0.1	< 2.5	< 0.04	< 2	< 0.1	< 0.005	< 0.4
Calcium	2000	160	840	42	4700	77	<60000	<3000	0.17	15
Chromium	37	2.9	56	2.8	115	1.9	110	5.2	0.05	4.4
Cobalt	95	7.5	110	5.4	270	4.4	< 24	< 1	< 0.2	< 20
Copper	28	2.2	30	1.5	33	0.54	156	7.4	0.05	4.4
Iron	2700	210	2440	120	8600	140	11600	550	1.1	97
Lead	NES	--	NES	--	NES	--	NES	--	< 0.05	< 4.4
Manganese	30	2.4	34	1.7	73	1.2	114	5.4	0.16	14
Mercury	< 0.04	< 0.003	< 0.08	< 0.004	< 0.1	< 0.002	< 0.08	< 0.004	< 0.005	< 0.4
Nickel	1000	79	1320	65	8800	140	12600	600	1.1	97
Selenium	< 2	< 0.2	< 4	< 0.2	< 5	< 0.08	< 4	< 0.2	< 0.01	< 0.9
Tellurium	< 50	< 4	< 100	< 5	< 125	< 2	< 100	< 5	< 0.3	< 30
Tin	< 100	< 8	< 200	< 10	< 250	< 4	< 250	< 12	< 1	< 90
Titanium	< 300	< 24	< 600	< 30	< 750	< 12	420	20	< 1	< 90
Vanadium	< 20	< 2	5800	290	14000	230	36900	1800	1.1	97
Zinc	3	0.24	174	8.6	300	4.9	2170	100	2.6	230
Chloride	< 28	< 2	< 53	< 3	NES	--	446	21	< 0.5	< 44
Fluoride	NES	--	274	14	323	5.3	< 1	< 0.05	< 0.1	< 9
Nitrates	49.5	3.9	35	1.7	NES	--	< 20	< 1	0.12	11
Sulfates	7890	620	12700	630	NES	--	19900	950	6.0	530
Total POM	NES	--	NES	--	NES	--	NES	--	NR	--
Total PCB	NES	--	NES	--	NES	--	NES	--	NR	--

See notes on Table 3-8.

TABLE 3-18. TRACE SPECIES AND ORGANIC EMISSIONS, SASS ORGANIC AND LIQUIDS SECTION COLLECTION

Test 19-4, Modified Boiler, Location 19, Low NO_x Condition

Sample Type	XAD-2 Resin		Organic Module Rinse		Condensate		Impinger No. 1		Impinger No. 2		Impinger No. 3	
Sample Number	535		19-4B		19-4C		Combined With Condensate		Combined With Condensate		Combined With Condensate	
Sample Weight/Vol.	150 g		535 ml		4460 ml							
Units	μg/g	$\mu g/m^3$	μg/ml	$\mu g/m^3$	μg/ml	$\mu g/m^3$	μg/ml	$\mu g/m^3$	μg/ml	$\mu g/m^3$	μg/ml	$\mu g/m^3$
Antimony	< 22	< 170	< 0.5	< 13	< 0.5	< 110						
Arsenic	6.2	47	< 0.005	< 0.1	< 0.005	< 1						
Barium	85	640	< 0.1	< 3	< 0.1	< 23						
Beryllium	< 0.45	< 3.4	< 0.005	< 0.1	< 0.005	< 1						
Cadmium	< 0.45	< 3.4	0.04	1	< 0.003	< 0.8						
Calcium	< B	0	=B	0	0.65	150						
Chromium	3.5	26	8.3	220	1.2	270						
Cobalt	=B	0	< 0.2	< 5	< 0.2	< 45						
Copper	6	50	0.54	14	0.08	17						
Iron	9	70	46	1200	3.1	700						
Lead	NES	--	< 0.05	< 1	< 0.04	< 9						
Manganese	0.8	6	0.62	17	0.08	17						
Mercury	< 0.02	< 0.2	< 0.005	< 0.1	< 0.005	< 1						
Nickel	< 2.2	< 17	20	540	3.2	700						
Selenium	< 0.89	< 7	< 0.01	< 0.3	< 0.010	< 2						
Tellurium	< 22	< 170	< 0.3	< 8	< 0.3	< 70						
Tin	< 45	< 340	< 1	< 30	< 1	< 225						
Titanium	< 130	< 980	< 1	< 30	< 1	< 225						
Vanadium	< 0.89	< 6.7	< 0.1	< 3	< 0.1	< 22						
Zinc	3.8	29	27	720	9.7	2200						
Chloride	4.5	34	< 0.5	< 13	27	6000						
Fluoride	=B	0	0.17	5	=B	0						
Nitrates	1.87	14	0.72	19	0.15	33						
Sulfates	449	3400	210	5600	9000 (SO_2)	$2x10^6$ (SO_2)						
Total POM	< 0.1	< 0.8	NES	--	NR	--						
Total PCB	< 1	< 8	NES	--	NR	--						

See notes on Table 3-8.

TABLE 3-19. TRACE SPECIES AND ORGANIC EMISSIONS, PROCESS SAMPLES AND MASS BALANCES

Test 19-4, Modified Boiler, Location 19, Low NO_x Condition

Sample Type	Emission in Partic. < 3 µm	Total Emission Concen.	Total Emission Rate	AA Analysis Input No. 6 Fuel Oil		AA Mass Balance	SSMS Analy. Test 19-3 No. 6 Fuel Oil	Mass Balance
Sample Number	734,540	SASS		19-4LF		Emission / Input	19-3LF	AA Emission / SS Input
Sample Weight/Vol.	1.2766 g	20.0 m^3	1.45 m^3/s	126 g/s			126 g/s	
Units	µg/m^3	µg/m^3	µg/s	µg/g	µg/s		µg/s	
Antimony	< 6	< 350	< 510	< 25	< 3200	< DL	< 30	< DL
Arsenic	3	55	80	< 2	< 250	> 0.30	51	1.60
Barium	41	800 < 850	1200	15	1900	0.63	510	2.30
Beryllium	< 0.14	< 6	< 9	< 0.3	< 38	< DL	< 30	< DL
Cadmium	< 0.14	1.1 < 6	1.6 < 9	< 0.3	< 38	> 0.04	< 30	> 0.05
Calcium	< 2900	440 < 460	640 < 670	< 10	< 1300	> 0.50	5500	0.12
Chromium	7.1	530	770	< 5	< 630	> 1.20	260	3.00
Cobalt	4.4 < 6	18 < 85	26 < 120	< 10	< 1300	> 0.02	260	0.10
Copper	8	95	140	< 3	< 390	> 0.40	190	0.74
Iron	690	3100	4500	30	3800	1.30	1800	2.50
Lead	NES	< 15	< 22	6	750	< 0.03	< 110	< DL
Manganese	6.6	65	94	< 0.5	< 63	> 1.50	58	1.62
Mercury	< 0.006	< 2	< 3	< 0.1	< 13	< DL	NR	--
Nickel	740	2200	3200	< 10	< 1300	> 2.50	2900	1.10
Selenium	< 0.3	< 11	< 16	< 1	< 130	< DL	110	< 0.15
Tellurium	< 7	< 290	< 420	< 25	< 3100	< DL	< 30	< DL
Tin	< 16	< 700	< 1000	< 25	< 3100	< DL	< 30	< DL
Titanium	20 < 32	20 < 1500	29 < 2200	< 250	<31000	> 0.001	130	> 0.22
Vanadium	2000	2400	3500	55	6900	0.54	19000	0.18
Zinc	100	3300	4785	< 5	< 630	> 8.00	320	15.00
Chloride	21	6000	8700	< 46	< 5800	> 1.50	190	46.00
Fluoride	5	24 < 33	35	41	5200	0.01	380	0.09
Nitrates	< 1	85	123	NR	--	--	--	--
Sulfates	950	21000	30000	NR	--	--	--	--
Total POM	NES	NES	NES	NR	--	--	--	--
Total PCB	NES	NES	NES	NR	--	--	--	--

See notes on Table 3-8.

However, SSMS analysis gave positive results for all these elements except mercury which was not reported. Mercury was detected by AA analysis in only one sample, the 10 μm cyclone sample on Test 19-3 (Table 3-13).

Analysis of fuel samples by AA produced many results that were below detection limits so that mass balances were not obtainable based on AA results alone. However, SSMS detection limits were lower than for AA and mass balances for most of the elements were obtained by combined use of both AA and SSMS results.

Duplicate analyses were performed on four SASS samples and all fuel samples. Results that were above detection limits were evaluated statistically by a paired t statistic test. This test indicated no statistically significant difference between the duplicate analyses. Out of a total of 85 pairs of concentration values in excess of detection limits only 15 duplicate result pairs differed by more than a factor of 2.

Table 3-20 compares the total trace species and organics concentrations as measured in the three tests conducted. Results by Atomic Absorption and Spark Source Mass Spectrometry are shown separately and the composite mass balances are shown. Arsenic, barium, and zinc emissions appear to be significantly higher for the two low NO_x tests by AA analysis as compared with the baseline test by AA. Cadmium, lead, chloride and fluoride emissions appear to be significantly lower for the low NO_x conditions. For the other elements emissions for all three tests are comparable.

The above conclusions for AA results are not completely consistent with SSMS results. Arsenic emissions by SSMS were nearly the same for baseline and low NO_x condition and are similar to the baseline emissions by AA. Barium and zinc were too high to be detected by SSMS for the baseline test. Cadmium emissions were lower for the low NO_x condition by SSMS and results are similar to the AA results. Lead emissions by SSMS were nearly the same at both conditions and comparable to baseline emissions by AA. Chloride emissions were higher for the low NO_x conditions by SSMS and for both tests, chloride emission was lower by SSMS than by AA. In contrast with the AA results, selenium emissions by SSMS were higher at the low NO_x condition compared to baseline and significantly higher than AA results.

TABLE 3-20. SUMMARY OF TOTAL TRACE SPECIES AND ORGANICS EMISSIONS FOR THE MODIFIED BOILER AT LOCATION 19 FIRING #6 FUEL OIL

	Total Emission Concentrations by Atomic Absorption, $\mu g/m^3$			Total Emission Concentrations by Spark Source Mass Spectrometry, $\mu g/m^3$		Best Mass Balances Using Either AA or SSMS Data		
Test	19-2	19-3	19-4	19-2	19-3	19-2	19-3	19-4
Condition	Baseline	Low NO_x	Low NO_x	Baseline	Low NO_x	Baseline	Low NO_x	Low NO_x
Antimony	< 380	< 540	< 350	11	160	--	--	< DL
Arsenic	6.5 < 15	59 < 64	55	6.5	6 < 12	0.26	1.7	1.60
Barium	95 < 210	640 < 740	800 < 850	MC	640	2.30	1.90	2.30
Beryllium	< 6	< 8.9	< 6	0.055 < 3	0.3 < 2	--	--	< DL
Cadmium	13	4.8 < 12	1.1 < 6	7.5 < 13	0.09 < 5	> 1.05	--	> 0.05
Calcium	650	2000	440 < 460	2000 < MC	67 < MC	0.80	0.55	0.12
Chromium	750	740	530	950	500	23.00	2.90	3.00
Cobalt	65 < 130	79 < 150	18 < 85	8 < MC	94	0.31	0.54	0.10
Copper	32	39 < 44	95	49	130	0.30	1.00	0.74
Iron	4300	4700	3100	1300 < MC	1100	1.35	0.89	2.50
Lead	45 < 70	9.9 < 21	< 15	52 < 67	54	0.83	--	< DL
Manganese	70	99	65	69	64	0.61	1.66	1.62
Mercury	< 1.9	0.06 < 21	2	NR	NR	--	--	--
Nickel	1300 < 1400	1600	2200	180 < MC	240 < MC	1.20	0.83	1.10
Selenium	< 12	9.9 < 290	< 11	2 < 5	100 < 110	--	1.40	< 0.15
Tellurium	< 300	< 450	< 290	0.04 < 3	0.2 < 3	--	--	< DL
Tin	< 750	< 1000	< 700	0.4 < 8	12	--	--	< DL
Titanium	70 < 1600	120 < 2500	20 < 100	53	580	0.92	1.40	> 0.22
Vanadium	3200 < 3400	3400 < 3600	2400	8 < MC	9 < MC	1.00	0.90	0.18
Zinc	370	810	3300	MC	680	1.30	1.60	15.00
Chloride	12000	3500	6000	4.3	2100	--	17.00	46.00
Fluoride	170 < 180	64 < 79	24 < 33	23	170	0.52	0.70	0.09
Nitrates	130	110 < 120	85	--	--	--	--	--
Sulfates	18000	18000	21000	--	--	--	--	--
Total POM	NES	50 < 51	NES	--	--	--	--	--
Total PCB	NES	< 7	NES	--	--	--	--	--

See notes on Table 3-8.

Mass balances for the baseline test were within a factor of two for ten elements. Arsenic, cobalt and copper were underbalanced (emission rate less than fuel input) by less than a factor of two. Barium and chromium were overbalanced (emission rate greater than fuel input) by more than a factor of two. For seven elements (antimony, beryllium, mercury, selenium, tellurium, tin and chloride) the values in both fuel and emissions were less than detection limits by both AA and SSMS so no mass balance could be obtained.

Mass balances for the first low NO_x test (19-3) were all within a factor of two except for chromium and chloride both of which were overbalanced in all three tests. Chromium might be expected to be overbalanced because of the stainless steel used in the SASS train. However nickel proved to be balanced within ± 20% for all three tests indicating no contamination by train stainless materials.

The observed increase in solid particulates, previously mentioned, of 30 to 60% for the low NO_x condition compared with baseline was reflected in the measured emissions of barium, chromium, cobalt, copper, iron, manganese, titanium, and zinc collected in the solid section of the SASS. Comparison of Test 19-3 (low NO_x) with Test 19-2 (baseline) indicates that calcium, chromium, iron, manganese, titanium, and zinc were increased by 20 to 90% in the solid particulate less than 3 μm. These same elements and also barium, cobalt and copper were increased by over 20% in the total amount of solid particulate collected. The other elements that could be detected did not appear to be increased in the solid particulate collected.

The use of three cyclones and a filter in the SASS train provides data on the enrichment of species on small particles. Particle surface area per unit mass increases as particle size decreases. Therefore species that condense on particle surfaces will be more concentrated on the smaller particles. Species that showed a definite enrichment include arsenic, cobalt, copper, iron, manganese, nickel, vanadium, zinc, chloride and sulfates. Species that showed no definite enrichment were calcium, chromium, fluoride, and nitrate. The remaining species were not present in sufficient quantities to allow an assessment.

Conclusions with regard to the inorganic species were that operation of this boiler with the combustion modifications implemented tended to produce an increase in emissions of certain inorganic species in rough proportion to the increase in solid particulate. Within the precision of the sampling methods there was no evidence to suggest any significant increases in emissions attributable to causes other than increased solid particulate emissions.

Organic species were difficult to identify. Most samples were of insufficient size to allow all inorganic and organic analyses to be performed. No polychlorinated biphenyls (PCB) were identified in any samples that could be analyzed for organics. With regard to total polycyclic organic matter (POM), there was an indication that POM increased at the low NO_x condition. Comparison of Table 3-14 with Table 3-10 shows that POM was present in the condensate at 0.5 $\mu g/m^3$ for the low NO_x condition but was below detection in the condensate for the baseline condition. However in both cases the POM was below detection by GC in the XAD-2 resin. The organic module rinse for the low NO_x condition (19-3, Table 3-14) contained the largest amount of total POM, 50 $\mu g/m^3$. Unfortunately there was insufficient organic module sample for the baseline test 19-2 so it is not possible to make a firm conclusion.

Since POM concentrations in the XAD-2 resins were below detection limits for gas chromatography, the XAD-2 samples were analyzed by gas chromatography-mass spectrometry (GC-MS). Analysis of the organic module wash by GC-MS might have also been informative. However, these samples were entirely consumed in performing other analyses. The results for the XAD-2 samples, Table 3-21, indicate a significantly lower level of total POM for the low NO_x test compared with baseline. Of the eight compounds required to be identified (Table 2-1), only three were detected as noted in the table. The fact that POM is lower in the XAD-2 for test 19-3 (Optimum Low NO_x mode), compared to baseline, is in contrast to the results for the organic module wash and condensate noted above.

TABLE 3-21. POM COMPOUNDS IN THE XAD-2 RESIN DETERMINED BY GAS CHROMATOGRAPH-MASS SPECTROMETRY, LOCATION 19

POM Component	Test 19-2, Baseline ng/g	ng/m^3	Test 19-3, Low NO_x ng/g	ng/m^3
Anthracene	3.2	24	0.45	3.4
Phenanthrene	--	--	0.02	0.1
*Methyl Anthracenes	0.2	1.6	0.12	0.9
Fluoranthene	1.2	9.0	0.13	0.9
Pyrene	0.05	0.4	0.05	0.4
*Benzo(c)phenanthrene	0.002	0.02	--	--
Chrysene	0.03	0.19	0.004	0.03
Benzo Fluoranthenes	0.007	0.05	0.007	0.05
*Benz(a)pyrene	0.004	0.032	--	--
Benz(e)pyrene	0.004	0.032	--	--
Total POM	4.74	35.5	0.78	5.8

*Compounds required to be identified for this contract

Note: Values in this table are expressed in nanograms (ng), (1 ng = 10^{-9} g). Values in other trace species and organics tables in this report are expressed in micrograms (μg), (1 μg = 10^{-6} g).

3.1.7 Boiler Efficiency

Boiler thermal efficiencies were determined by the ASME Heat Loss Method using on-site measurements of the fuel and flue gas compositions. The efficiency of steam generating equipment determined within the scope of the ASME Code is the gross efficiency and is defined as the ratio of the heat absorbed by the working fluid to the heat input. This definition disregards the equivalent heat in the power required by the auxiliary apparatus external to the envelope. The abbreviated efficiency calculation considers only the major heat losses and only the chemical heat in the fuel as the input.

Location 19 Boiler Efficiency

Baseline Condition--

Thermal efficiency was measured at baseline conditions with the boiler firing #2 and #6 oil and natural gas. A baseline measurement was made at the start of the test series and each day prior to combustion modification tests. With #2 oil and #6 oil the thermal efficiency at baseline condition was 82.5%. The baseline thermal efficiency of the boiler when firing natural gas was 79.2%

Effect of Excess Air--

The effect of low excess air firing is shown in Figure 3-17 where boiler thermal efficiency as a function of stack gas oxygen content is plotted for natural gas fuel. Two burner configurations, a ring burner and a gas gun burner, were tested. The effect of excess O_2 on efficiency was similar for both burners, but the gas gun showed higher efficiency over the range of O_2. Decreasing the excess oxygen from the baseline condition of 3.2% O_2 to 2.0% resulted in an efficiency increase of 0.8% due to lower stack losses. A further decrease in O_2 to 1.1% (where CO increased drastically) led to only an additional 0.1% increase in efficiency.

The effect of excess oxygen on boiler thermal efficiency is illustrated in Figure 3-18 for #2 oil firing and in Figure 3-19 for #6 oil firing. With #2 oil, decreasing the excess O_2 from the baseline value of 3.05% to 0.6% O_2

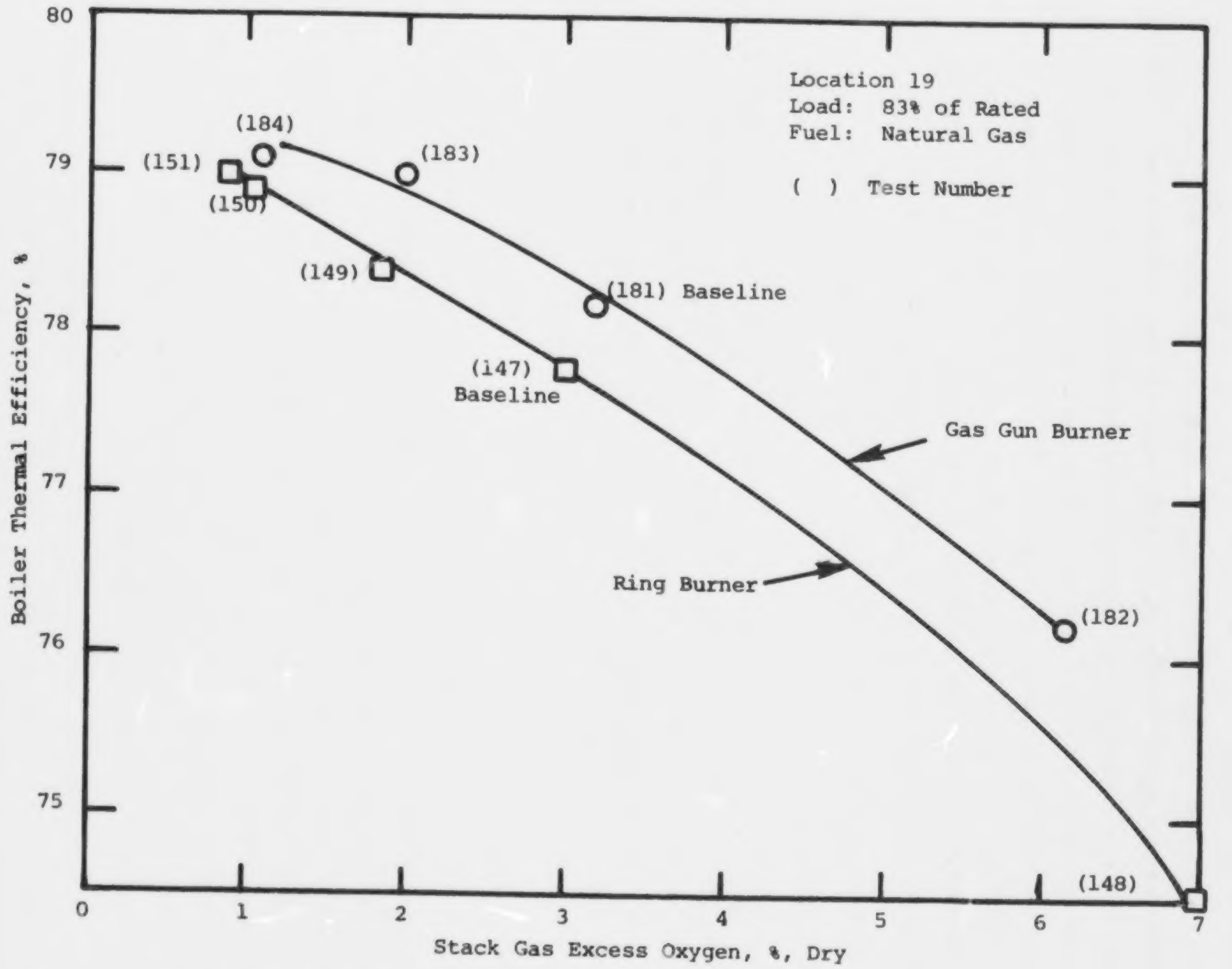

Figure 3-17. The effect of excess oxygen on boiler thermal efficiency for a watertube boiler.

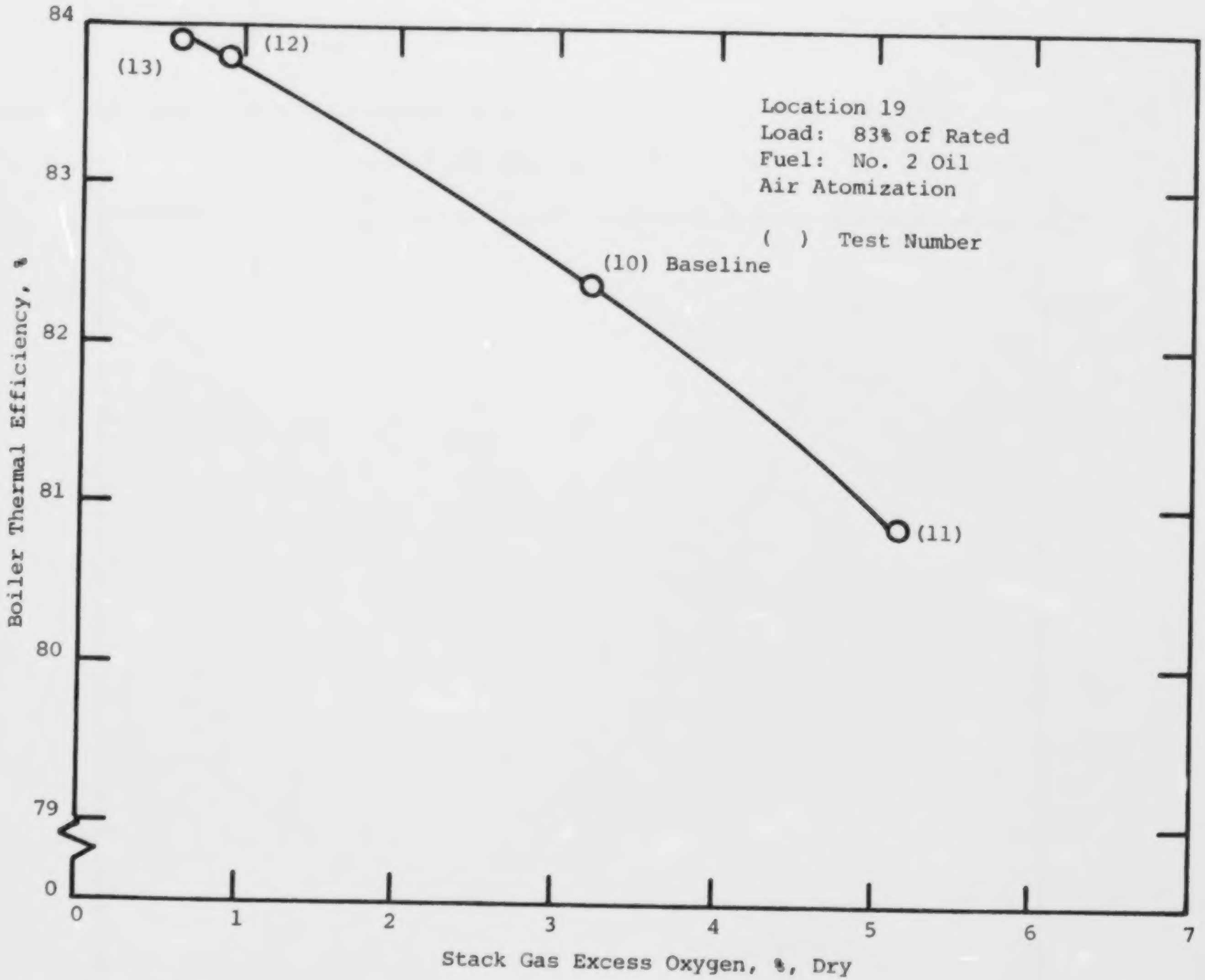

Figure 3-18. The effect of excess oxygen on boiler thermal efficiency (#2 oil).

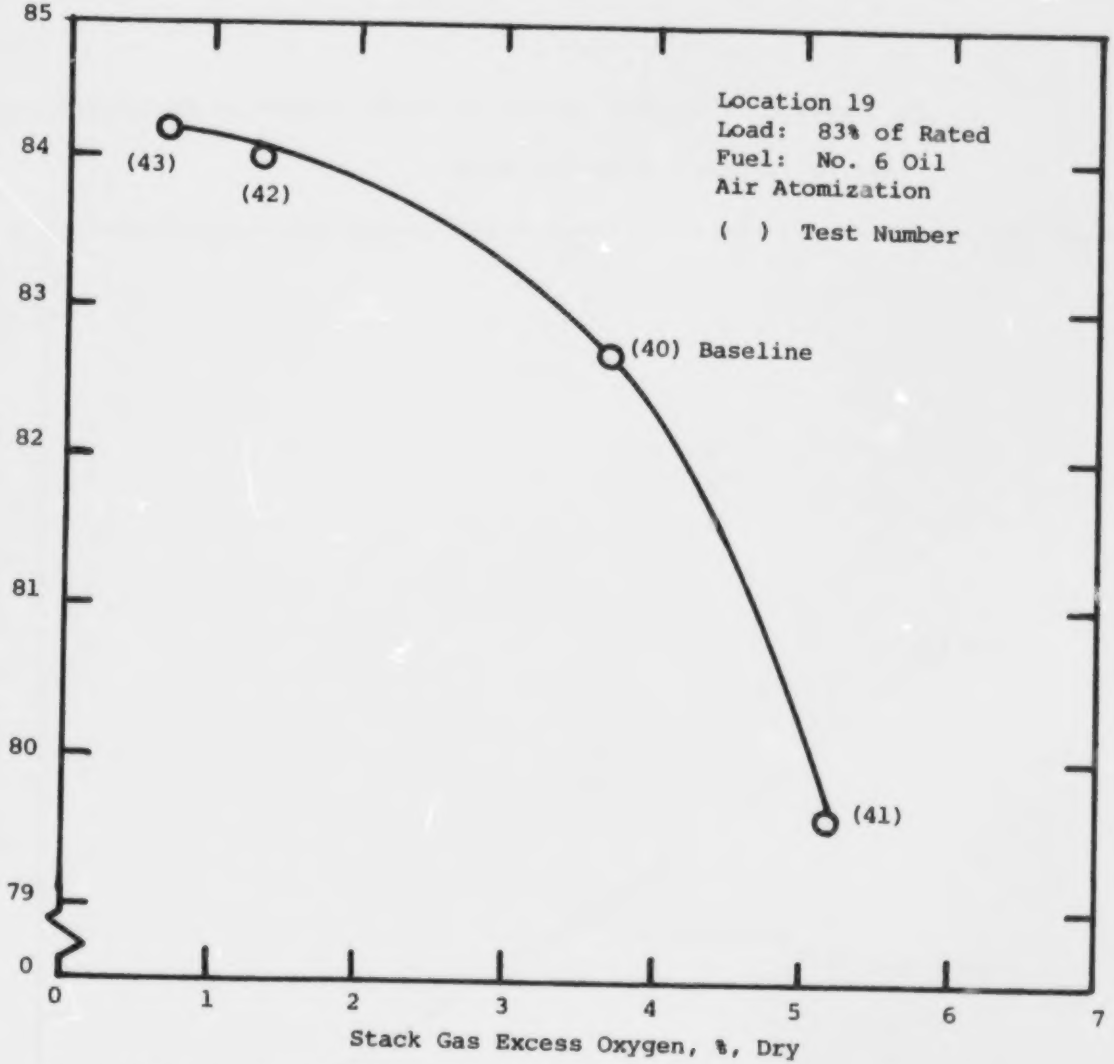

Figure 3-19. The effect of excess oxygen on boiler thermal efficiency (#6 oil).

resulted in an increase in thermal efficiency of 1.9%. Decreasing the O_2 from 0.9% to 0.6% (the high CO threshold) resulted in a minimal increase in efficiency of 0.1%. With #6 oil, only 0.2% increase in efficiency was realized when the O_2 decreased from 1.3% to 0.7%.

In general, the efficiency increased 1-2% when the O_2 was lowered to near the CO threshold from the baseline O_2 condition for all test fuels. Peak efficiency for oil fuels was approximately 84% at 0.7% O_2 and 79% at 1% O_2 for natural gas.

Effect of Staged Combustion Air--

Boiler thermal efficiency was calculated using measurements taken during the staged combustion air parametric tests. The depth at which the secondary air was injected was varied as was the ratio of burner air to secondary air. When firing #2 oil, a very slight change in efficiency was noted as the injection point was varied. The influence of injection point on efficiency is illustrated in Figure 3-20 for #2 oil. These data show an increase of only 1/2% from the baseline condition as the injection point is varied to the maximum distance of 7 feet with a burner equivalence ratio of approximately 1. Slightly greater increases are noted for burner equivalence ratio of 1.1 (fuel rich). All data are at approximately the same operating condition of 3% excess O_2. When firing #6 oil and natural gas, no measurable change was noted as injection depth was varied. The only change in boiler thermal efficiency was due to changes in excess O_2.

Effect of Flue Gas Recirculation--

The effect of flue gas recirculation on boiler efficiency is shown in Figures 3-21 through 3-23 for #2 oil, #6 oil, and natural gas respectively. Figure 3-21 shows the change in efficiency, normalized to the baseline efficiency as a function of the percent of flue gas recirculated to the burner for #2 oil firing. These data indicate that boiler efficiency is more sensitive to changes in flue gas recirculation when the boiler is operating at the normal O_2 level of 3% than when operating in the low O_2 mode. When the recirculated flue gas approaches 25% of the total, the boiler efficiency drops by approximately 3%. In the low O_2 mode (∿ 1% excess O_2), the degradation in efficiency due to 25% recirculated flue gas is only 1.5%.

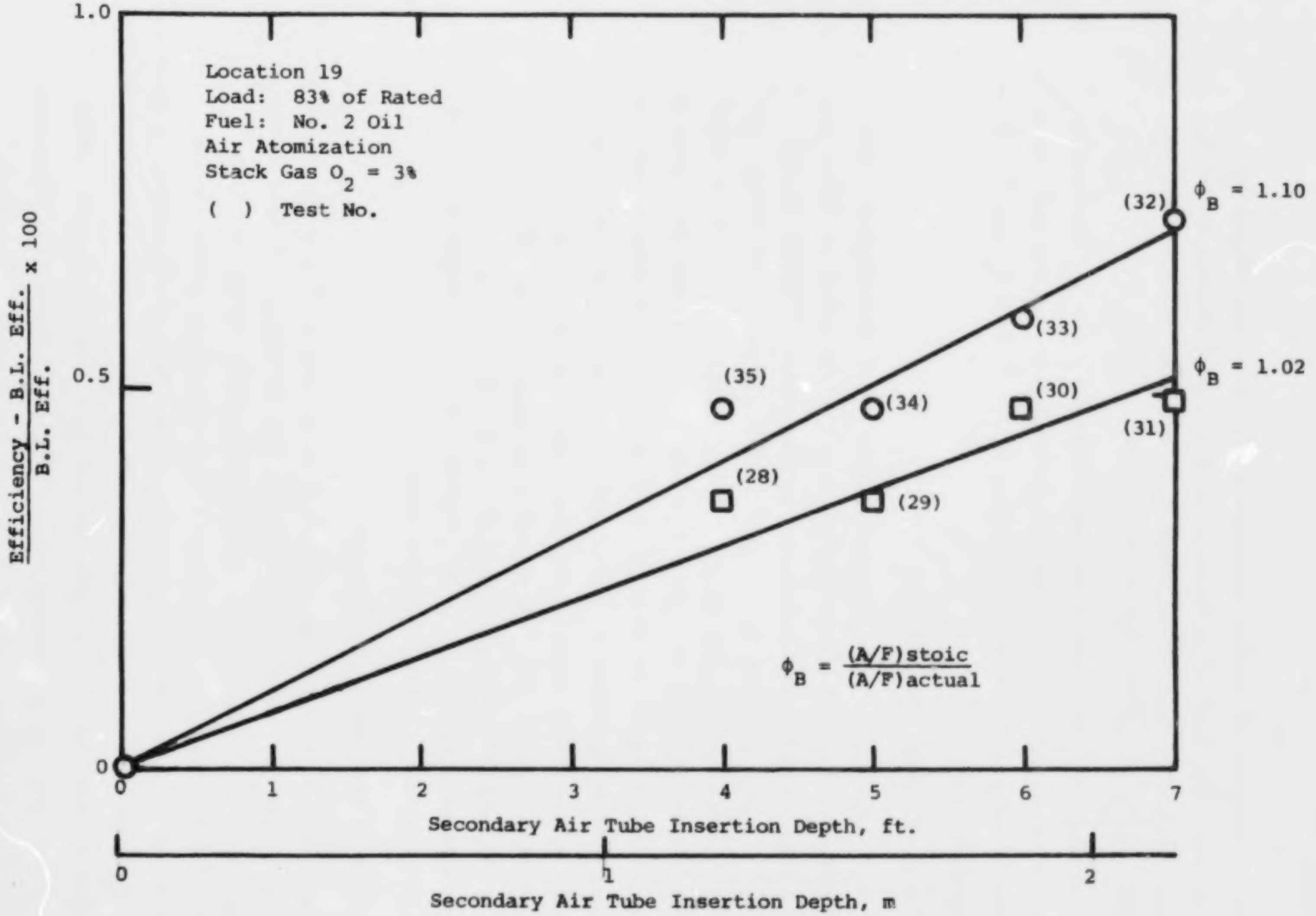

Figure 3-20. The effect of secondary air insertion depth on boiler thermal efficiency (#2 oil).

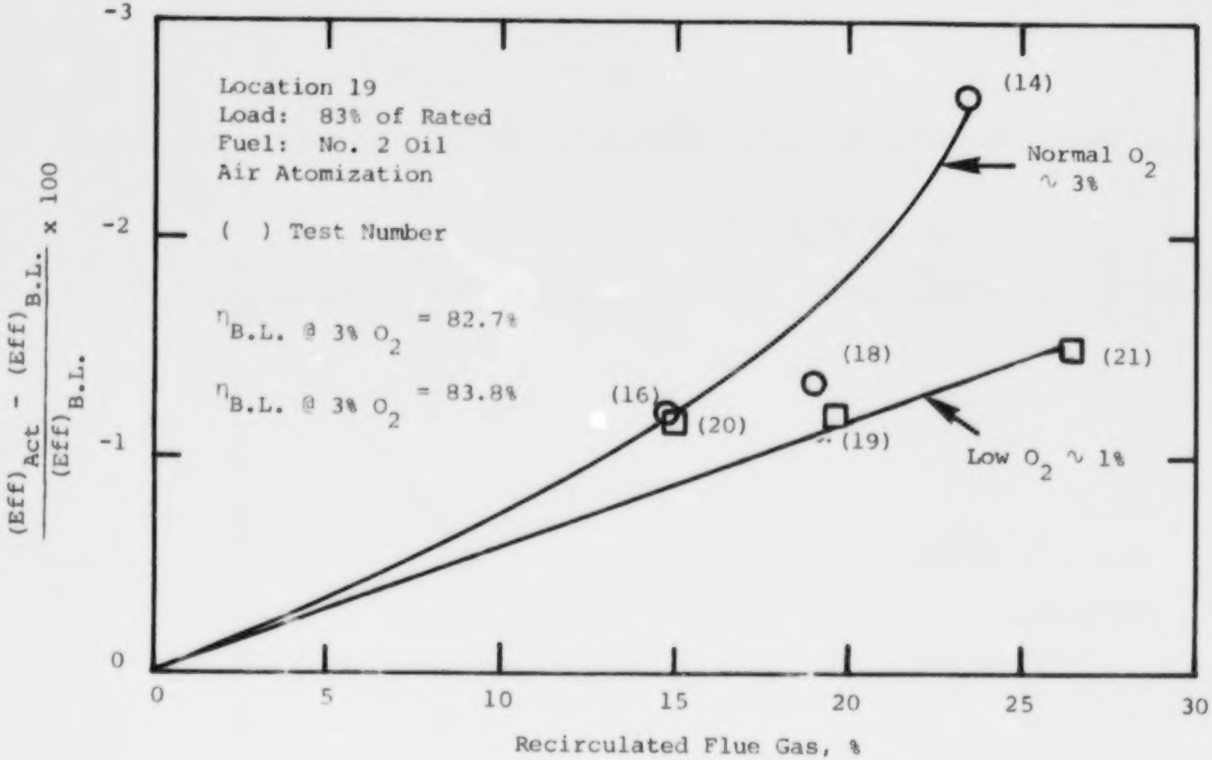

Figure 3-21. The effect of flue gas recirculation rate on boiler thermal efficiency (#2 oil).

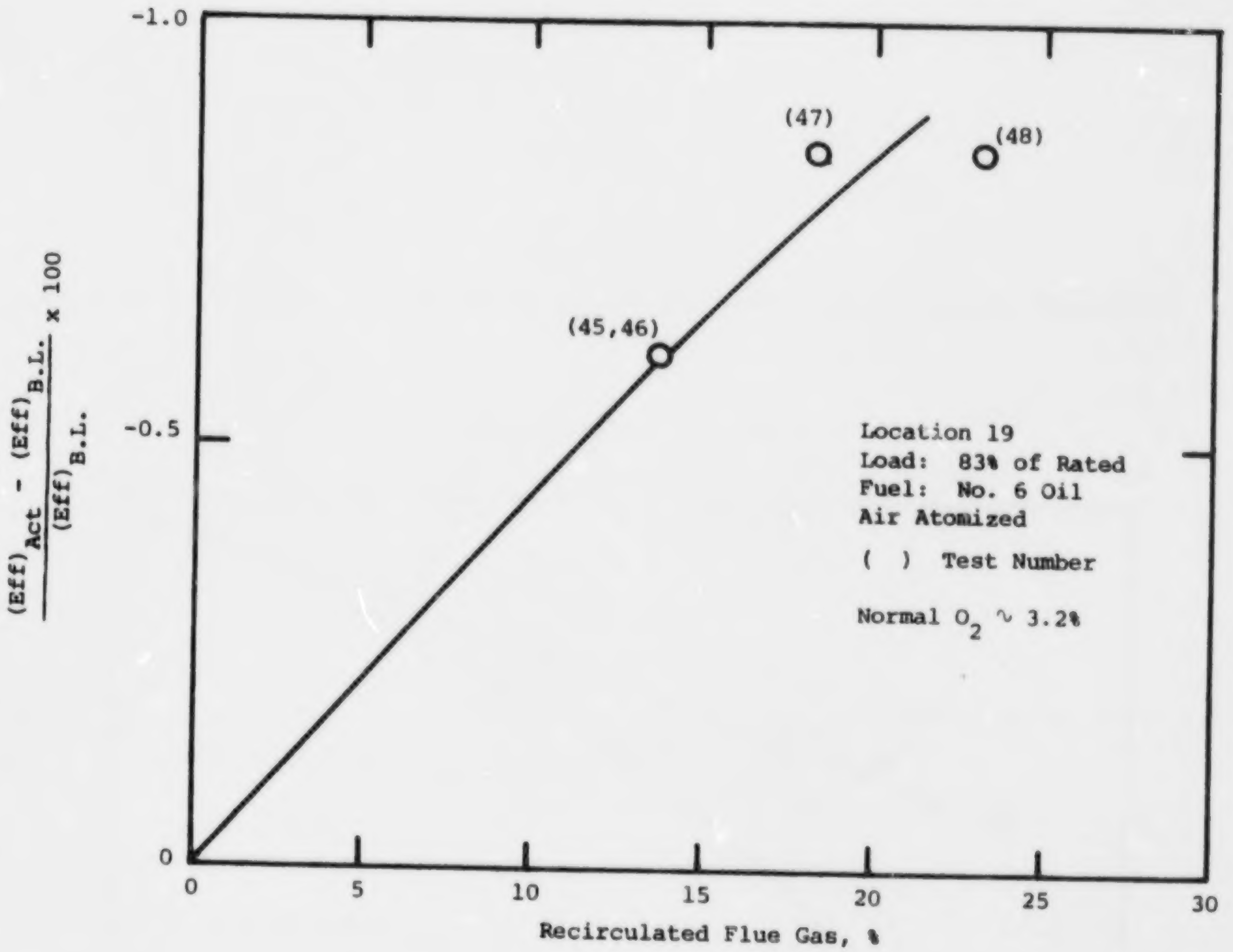

Figure 3-22. The effect of flue gas recirculation rate on boiler thermal efficiency (#2 oil).

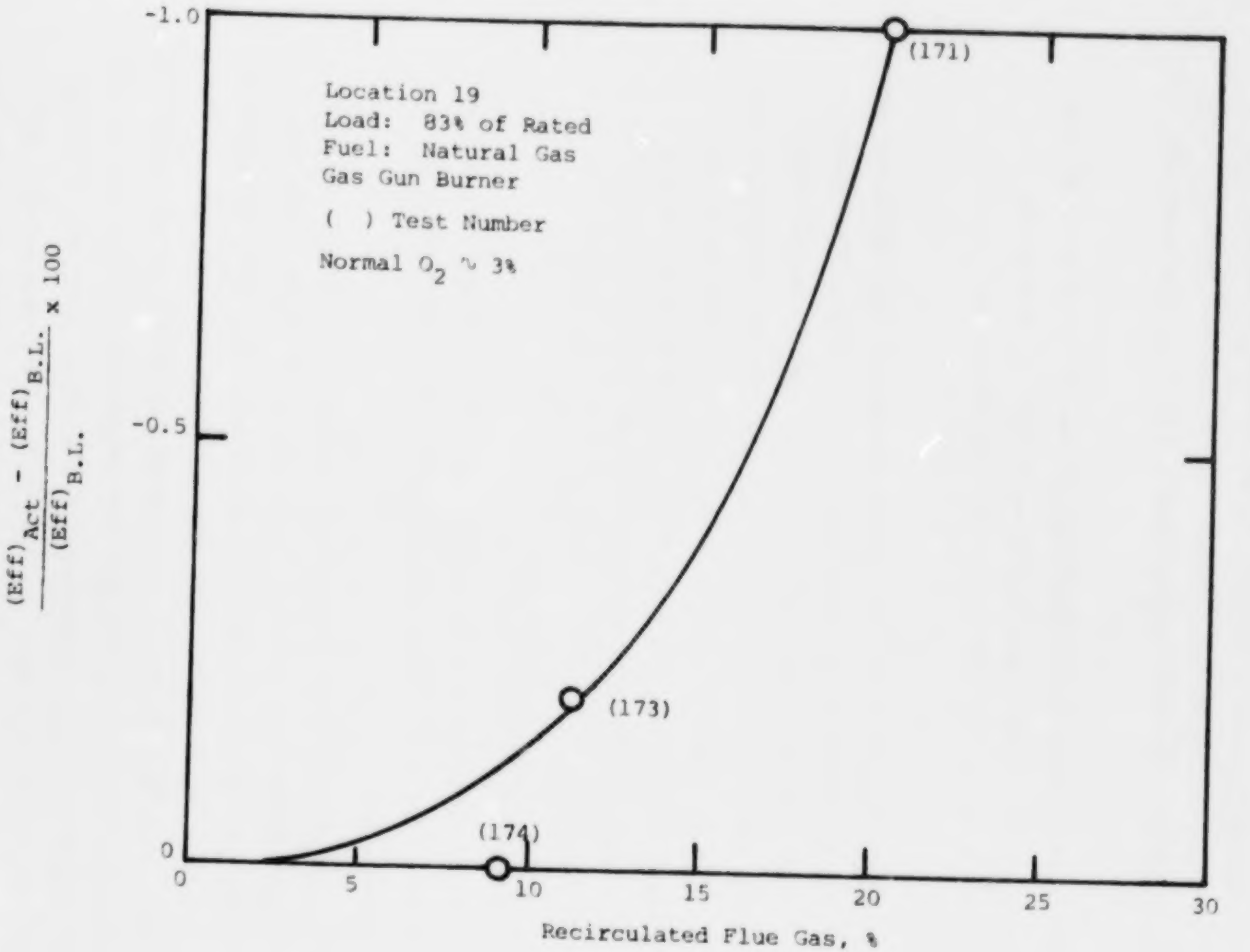

Figure 3-23. The effect of flue gas recirculation rate on boiler thermal efficiency (natural gas).

On an absolute basis, the boiler efficiency is approximately 1% higher when operating in the low O_2 mode with flue gas recirculation than operation at the normal O_2 level.

Efficiency degradation as a function of percent recirculated flue gas is shown in Figure 3-22 for #6 oil firing. At the maximum recirculation rate, boiler efficiency was degraded approximately 0.8% from the baseline condition.

Figure 3-23 illustrates efficiency degradation as a function of flue gas recirculation rate for natural gas firing at normal O_2 conditions. Maximum recirculation rate of 20% results in an efficiency loss of approximately 1%.

The effects on efficiency of the various combustion modifications and combinations of the modifications are tabulated in Table 3-22. The values enclosed in boxes represent the lowest NO_x condition. With the oil fuels, the low NO_x condition was with flue gas recirculation, staged combustion air and low excess air firing. With #2 oil, operation in this mode resulted in an efficiency degradation of 0.8% and with #6 oil the efficiency increased 0.1%. Natural gas firing in the low NO_x mode (FGR and low O_2) resulted in an efficiency penalty of 0.4%.

3.1.8 Conclusions From Location 19 Tests

The test series conducted on the watertube boiler at Location 19 permitted an evaluation of several combustion modification techniques using #2 and #6 oil and natural gas.

Combustion modifications evaluated were lowered excess air, flue gas recirculation, staged combustion air, and combinations of these. The data presented previously in Table 1-1 show the reduction in NO_x from the baseline condition as a function of combustion modification technique and type of fuel. These data indicate that for oil fuel, the combination of all three combustion modification techniques results in the greatest reduction in NO_x. For natural gas, the maximum reduction occurs with the combination of flue gas recirculation and low O_2. NO_x reductions were greatest with #2 oil and natural gas which showed 77% and 79% reductions respectively. A 53% reduction in NO_x was achieved while firing #6 oil using FGR, staged air, and low O_2.

TABLE 3-22. SUMMARY OF CHANGE IN BOILER EFFICIENCY DUE TO COMBUSTION MODIFICATIONS

Boiler Operating Mode	No. 2 Oil	No. 6 Oil	Natural Gas
Low O_2	+ 1.5%	+ 1.5%	+ 0.9%*
SCA, Normal O_2	+ 0.9%	+ 0.1%	+ 0.6%*
SCA, Low O_2	+ 1.1%	+ 0.8%	+ 0.6%$^+$
FGR, Normal O_2	- 1.9%	- 0.7%	- 0.8%$^+$
FGR, Low O_2	+ 0.9%	+ 0.6%	$\boxed{-\ 0.4\%^+}$
FGR + SCA, Normal O_2	- 1.2%	- 0.8%	- 0.5%*
FGR + SCA, Low O_2	$\boxed{-\ 0.8\%}$	$\boxed{+\ 0.1\%}$	§

*Optimized gas gun

$^+$Ring burner

§Stability limits prevented lowering O_2

Indicates lowest NO_x condition ☐

Table 1-2 presented the results of particulate measurements using EPA Method 5 for the boiler under baseline operation in each modified condition and for each fuel. The lowest particulate emissions also occur at the same condition as the low NO$_x$ mode.

3.2 LOCATION 38 COMBUSTION MODIFICATIONS

The test program was conducted during the period of May 3 through June 11, 1976. The test unit was a watertube boiler operating on #6 fuel oil and natural gas at a nominal load of 40,000 lb/hr steam flow. The design capacity was 45,000 lb of steam flow per hour. The testing consisted of measuring gaseous and particulate emissions at three different modes of operation and comparing these emissions to baseline operation. The modified modes of operation were staged combustion, variable preheater temperature and excess air variations. Combinations of these variables were also evaluated.

Gaseous emissions were measured for both fuels with the exception of SO$_x$ which was only measured with #6 oil. Particulate emissions measurements were only performed with #6 fuel oil. Table 3-23 presents a summary of emission data at modified conditions as well as baseline conditions.

The gaseous emissions were sampled at the boiler exit prior to the air heater just as was done during baseline testing. Cold line data was used as the primary NO value since some problems with the heated line were encountered during the testing.

Excess air variations, variable preheat, windbox register vane setting variation and staged combustion air tests were conducted.

The side walls of the boiler tested were fitted with a series of opposing ports at five locations which ranged in distance from less than 100 to more than 300 centimeters from the furnace front (Fig. 2-4). Separate fan and duct work was provided to allow a fraction of the total boiler air flow to be admitted at these ports to give staged or secondary combustion. The relative air flows entering the boiler through the burner and through the secondary air ports were determined from velocity profiles taken in the fan inlet ducts using a standard pitot tube. It should also be noted that

TABLE 3-23. SUMMARY OF LOCATION 38 COMBUSTION MODIFICATION TEST DATA

Test No.	Date 1976	Load kg/s (10^3 lb/hr)	Fuel	O_2 (%)	NO_x ng/J (ppm)	NO ng/J (ppm)	CO ng/J (ppm)	CO_2 %	HC ng/J (ppm)	SO_2 ng/J (ppm)	SO_3 ng/J (ppm)	Particulate Total ng/J (lb/MMB)	Particulate Solid ng/J (lb/MMB)	Stack Temp. K (°F)	Eff. (%)	Comments
200G-2	6/2	5.04 (40.0)	NG	1.60	*	82.1 (161)	43.3 (140)	10.5	*	--	--	--	--	497 (434)	81.2	Baseline
201G-5	6/2	4.94 (39.2)	NG	1.25	*	70.9 (139)	>619 (>2000)	10.5	*	--	--	--	--	494 (430)	81.4	O_2 swing, Port 14 & 15
204-9	6/7	4.91 (39.0)	NG	2.25	*	56.6 (111)	37.8 (122)	10.5	*	--	--	--	--	497 (435)	80.8	Staged combustion air
205-4	6/8	4.98 (39.5)	NG	2.2	*	62.2 (122)	3.1 (10)	10.5	*	--	--	--	--	514 (465)	80.2	Variable preheat (VPH)
200G-19	6/11	4.98 (39.5)	NG	1.98	*	66.8 (131)	--	10.5	*	--	--	--	--	492 (425)	81.2	Windbox register adjustment
204-18	6/9	5.04 (40.0)	NG	2.25	*	52.5 (103)	85.1 (275)	10.5	*	--	--	--	--	506 (450)	80.4	Constant SCA, variable FD fan, Ports 14 & 15 open
204/5-30	6/11	4.91 (39.0)	NG	2.25	*	24.0 (47)	17.3 (56)	10.25	*	--	--	--	--	564 (556)	78.0	SCA multiple port variation with APH bypass, Ports 14 & 15, 6 & 7
200-24	5/24	4.79 (38.0)	#6	2.9	*	145.9 (286)	7.5 (22)	13.8	*	737.3 (944)	21.9 (28)	66.4 (.154)	36.6 (.085)	501 (442)	84.8	Baseline, particulate, impactor, SO_x
201-12	5/25	4.89 (38.8)	#6	1.55	*	115.3 (226)	22.2 (65)	15.0	*	740.4 (948)	10.9 (14)	47.6 (.110)	38.3 (.088)	493 (427)	85.6	Low O_2, particulate, SO_x
202-4	5/25	4.28 (34.0)	#6	2.6	*	132.1 (259)	10.9 (32)	14.1	*	--	--	54.4 (.126)	37.6 (.087)	511 (550)	82.0	VPH, particulate, SO_x
203-26A	5/20	4.79 (38.0)	#6	3.3	*	97.4 (191)	21.1 (62)	13.0	*	788.8 (1010)	10.9 (14)	52.6 (.122)	38.7 (.09)	491 (424)	85.0	SCA, particulate, SO_x
203-26B	5/20	4.91 (39.0)	#6	3.1	*	--	34.1 (100)	13.0	*	--	--	62.2 (.144)	39.9 (.092)	492 (416)	85.0	SCA, particulate
201-15	5/27	4.89 (38.8)	#6	1.6	*	128.0 (251)	--	15.0	*	781.0 (1000)	28.1 (36)	43.7 (.101)	38.7 (.089)	494 (430)	85.6	Low O_2, particulate
203-15	5/17	4.73 (37.5)	#6	3.0	*	86.0 (153)	39.9 (117)	12.1	*	--	--	--	--	498 (436)	84.9	Constant SCA, variable FD fan, Port 14 & 15
203-22B	5/18	4.66 (37.0)	#6	2.8	*	91.0 (162)	34.1 (100)	12.0	*	--	--	--	--	508 (455)	84.6	SCA multiple port variation 14 & 15 open, 12 & 13 10% open

* Heated line malfunction prevented measurement of NO_x and HC data.

the secondary air fan delivered essentially ambient (boiler room) temperature air into the boiler compared to the preheated burner air flow. Thus, the influence of reduced air temperature as well as staged combustion must be considered when evaluating the NO trends.

A gaseous emission traverse was conducted at the boiler outlet for both fuels. Figures 3-24 and 3-25 show the variation in emission values versus probe insertion depth. The graphs indicated an O_2 variation across the duct that increases on the east and west walls. The O_2 variation is approximately 2% for baseline conditions for either fuel. The high O_2 values near the walls indicate furnace air leakage especially since the NO distribution does not follow the O_2 distribution in the duct. The sample probe was installed at the center of the boiler outlet duct where there was no interference of wall air leakage.

3.2.1 Location 38 Baseline Tests

Baseline emissions measurements were made with the boiler in the "as found" condition firing #6 fuel oil. Subsequent baseline tests were made with the boiler firing natural gas. Baseline measurements were made at the start of each series of combustion modification tests. The boiler load was constant at approximately 89% of rated load for all tests.

The measured baseline NO_x emissions when firing #6 oil were 167.5 ng/J (298 ppm). The baseline NO_x values for natural gas were measured at 82.1 ng/J (161 ppm). Baseline particulates were 66.4 ng/J (0.154 lb/MMBtu). Particulate size distribution was also measured at baseline conditions. The baseline size distribution indicated that more than 90% of the particulate was 3 micrometers diameter or less. Analyses of the #6 fuel oil and natural gas are presented in Tables 3-24 and 3-25.

The heated sample line was not operating during the test series so that only cold line NO data are recorded. The hydrocarbon data are also not reported because the hot line malfunctioned.

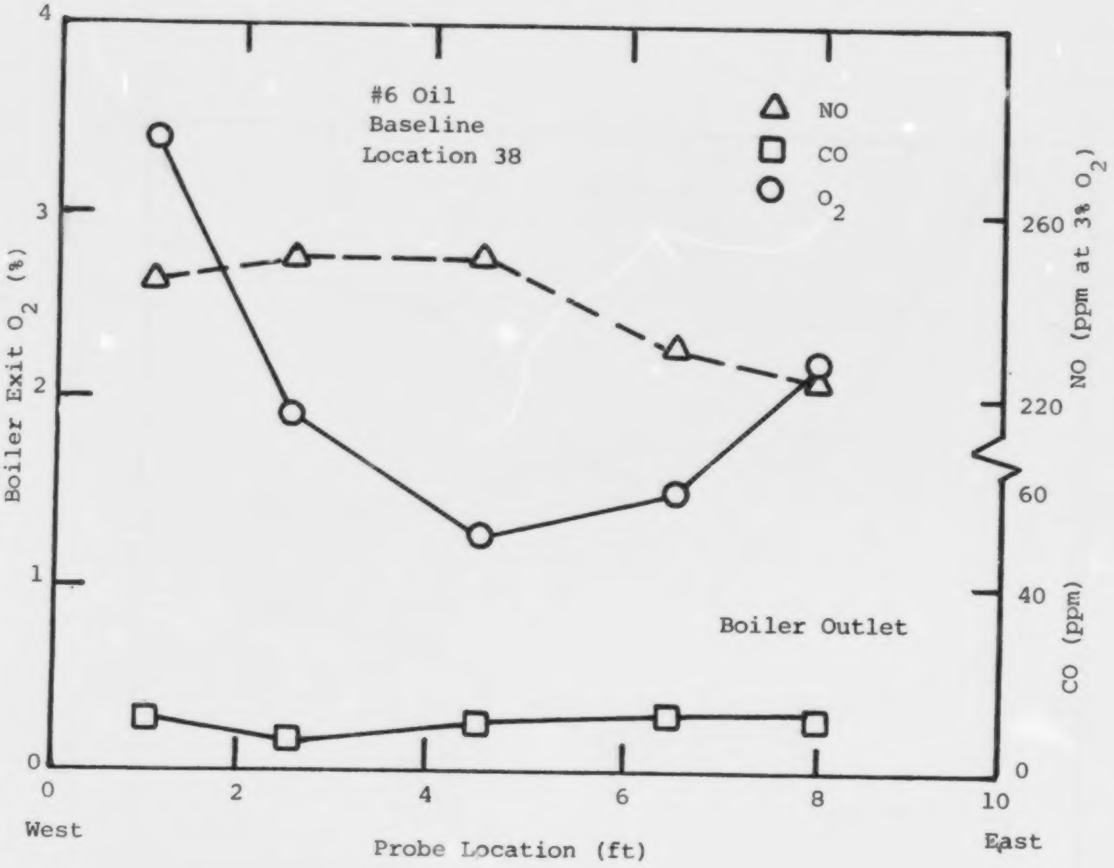

Figure 3-24. Emission traverse while firing #6 oil.

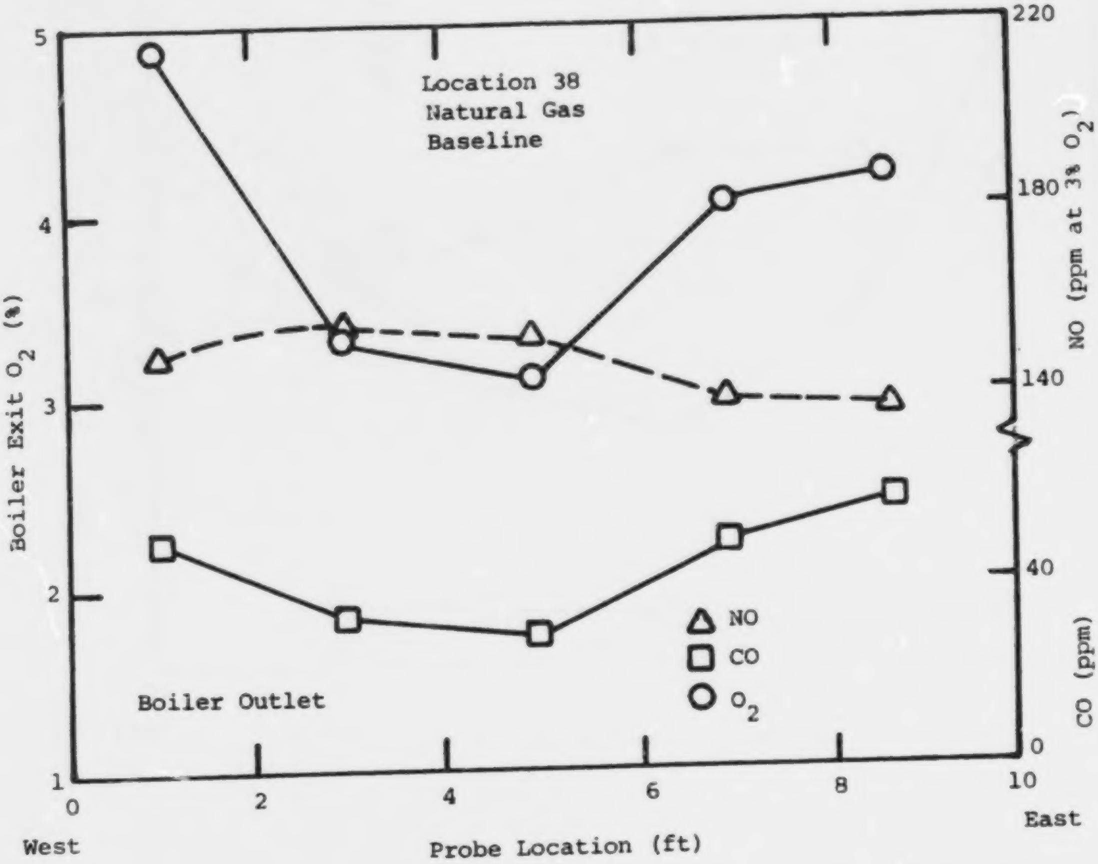

Figure 3-25. Emission traverse while firing #6 oil.

TABLE 3-24. SUMMARY OF LOCATION 38 FUEL OIL ANALYSES

Laboratory No.	G3393	G3430
Carbon, %	86.21	86.26
Hydrogen, %	11.22	11.20
Nitrogen, %	0.32	0.30
Sulfur, %	1.88	1.88
Oxygen, %	0.34	0.29
Ash, %	0.03	0.07
API Gravity	15.2	15.2
HHV, Btu/lb	18,449	18,484

TABLE 3-25. LOCATION 38 NATURAL GAS ANALYSIS

Oxygen, %	0.00
Nitrogen, %	0.28
Carbon Dioxide, %	0.60
Methane	96.99
Ethane	1.98
Propane	0.10
Butanes	0.04
Pentanes	0.01
Hexane	0.00
Heating Value, Btu/SCF (Dry)	1011

3.2.2 Combustion Modifications With #6 Oil

- Excess Air Variations--

The effect of excess oxygen on NO emissions is shown in Figure 3-26 for the unit firing #6 oil. The excess oxygen varies from a low value of 1.25% to a high value of 4.4%. Baseline O_2 for this test series was found to be at 2.5% with 221 ppm NO at 3% O_2 dry. At the low O_2 setting of 1.25%, CO values of approximately 950 ppm were measured. Increasing the air flow to 1.6% O_2 decreased CO emissions to approximately 80 ppm.

- Variable Preheat (VPH)--

Figure 3-27 shows the effect of windbox temperature on NO emissions for #6 oil. The graph shows a considerable decrease of NO with reduced combustion air temperature. The high windbox temperature is obtained with a steam coil air heater located between the FD fan and the normal regenerative air heater. Windbox temperature is lowered with a bypass duct and damper which redirect the FD exit flow either partially or totally around the air/flue gas heat exchanges. The test series was conducted at a load of 85% of rated load with approximately 2.55% excess oxygen. The NO decreased by 2.75 ppm/10 °F windbox temperature reduction.

- Staged Combustion Air (SCA)--

The data of NO_x versus staged combustion air port location for oil fuel (at a nominal ratio of SCA to total air flow of 14%) indicates that the most effective location for staged air is the farthest from the burner, ports 14 and 15 (Fig. 3-28). Ports 14 and 15 are the same distance from the burner as ports 12 and 13 but are 40 inches higher. Ports 12 and 13 are the next most effective and the effectiveness decreases as the distance from the burner diminishes.

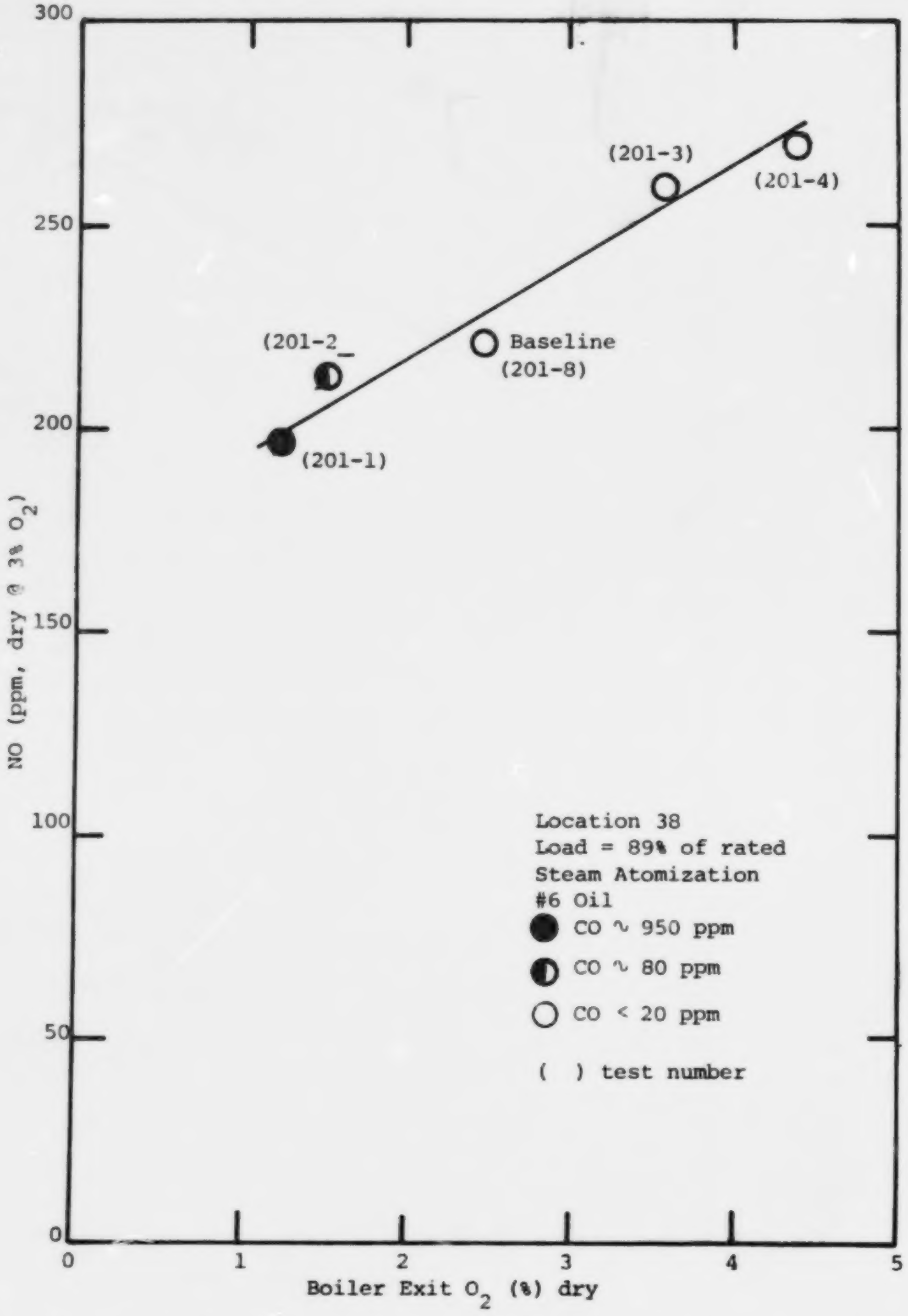

Figure 3-26. The effect of excess oxygen on NO emissions (#6 oil).

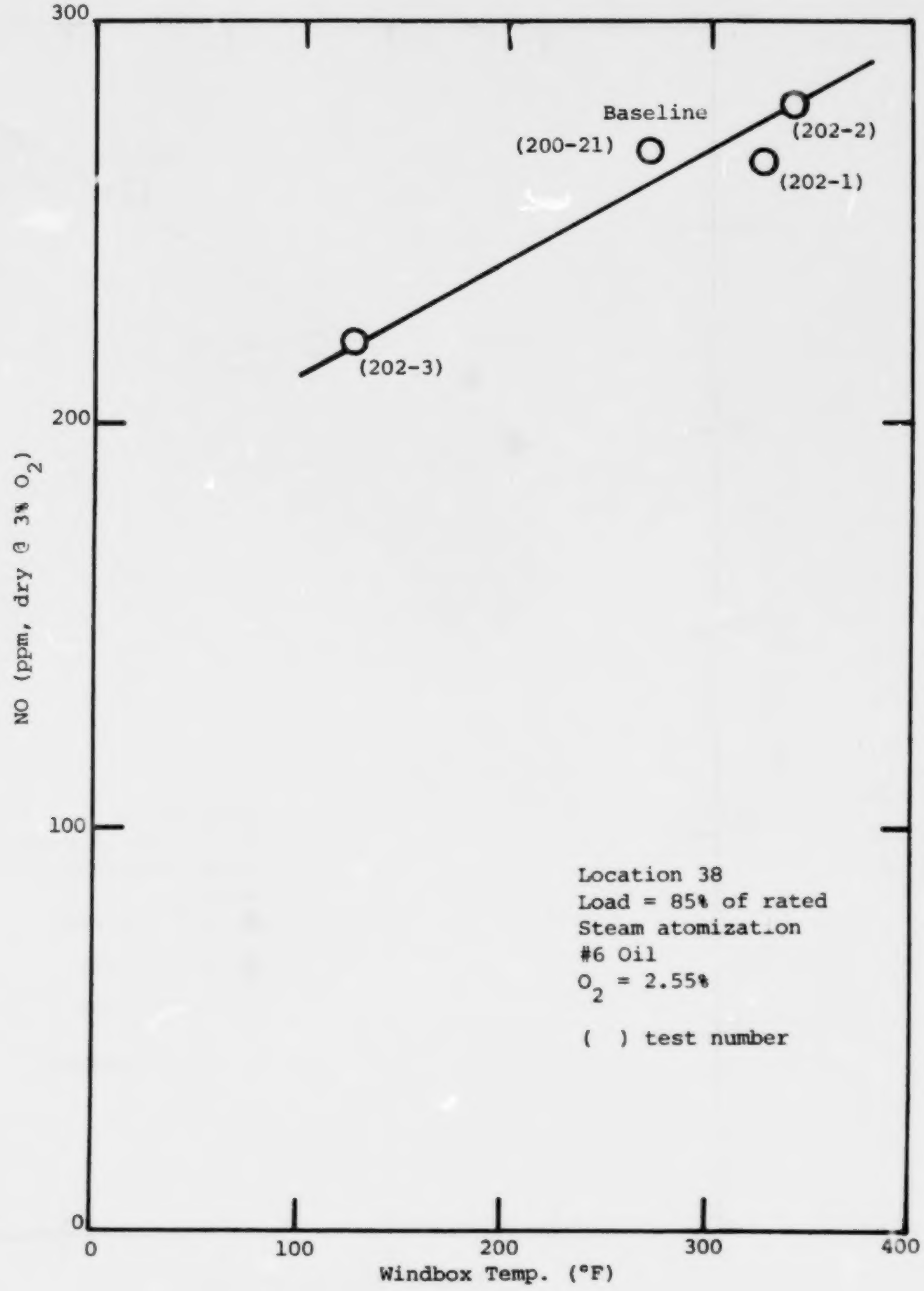

Figure 3-27. The effect of windbox temperature on NO emissions (#6 oil).

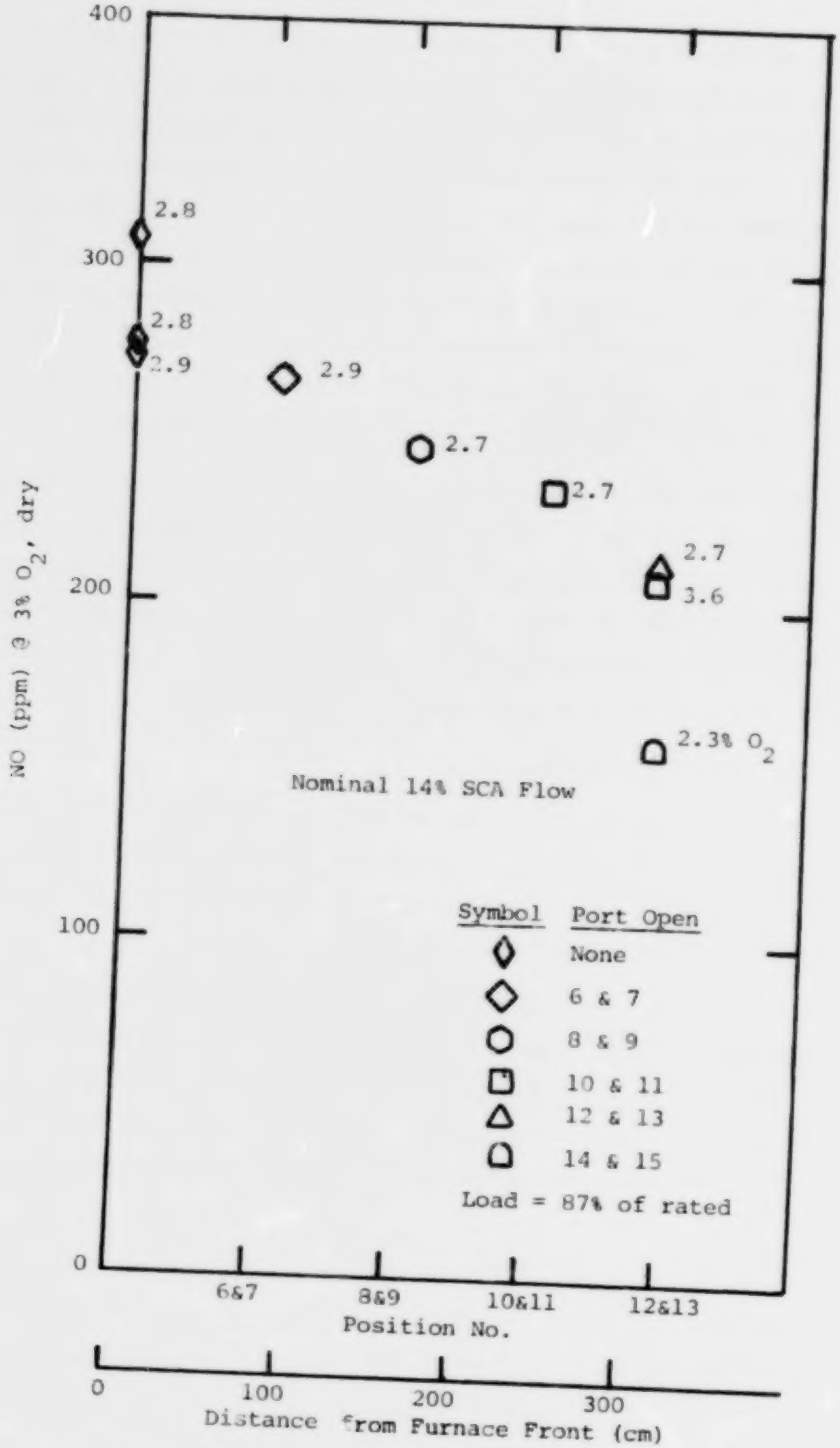

Figure 3-28. NO versus SCA - port location for #6 oil fuel.

A further series of tests was conducted to evaluate the sensitivity of NO emissions to burner stoichiometry. For these tests both the total boiler air flow and the fraction of the total air flow entering through the SCA ports were varied by (1) fixing the forced draft (FD) fan flow and reducing the SCA flow and (2) by fixing the SCA flow and varying the FD fan flow. The data are shown in Figure 3-29 for #6 oil fuel. The lowest NO level is obtained at the minimum burner air flow. This trend is more readily observable when the NO data are presented as a function of the percent of stoichiometric air at the burner as shown in Figure 3-30. The oil data in Figure 3-30 correlates the data from Figure 3-29 and illustrates as well the effect of SCA port location.

The multiple port variations of the staged combustion air with the boiler firing #6 fuel oil (Fig. 3-31) shows a similar trend as the single port 14 and 15 operation. The only multiple ports tested were combinations of ports 12 and 13 with ports 14 and 15 and little further reduction was observed. There appears to be no advantage to running lower than stoichiometric air through the burner with these test conditions.

3.2.3 Particulate and SO_x Testing

Particulate, particulate size, and sulfur oxides measurements were made with the boiler operating on the #6 fuel oil. Measurements were made with the boiler operating in the baseline condition and with lowered excess O_2, variable air preheat and staged combustion air.

A summary of the Method 5 particulate measurements is presented in Table 3-26. These measurements indicate that lowered excess air resulted in the lowest total particulate emissions. All combustion modifications resulted in lower total particulate measurements than the baseline condition, but solid particulate emissions for all combustion modifications were higher than for baseline.

SO_x emissions were measured for baseline, low O_2, staged combustion air and variable preheat operation using the Shell-Emeryville absorption-titration method. Three samples were normally taken for each operating condition. The data obtained for the variable preheat tests are not reported due to sampling error. The remaining data are presented in Table 3-27. The data

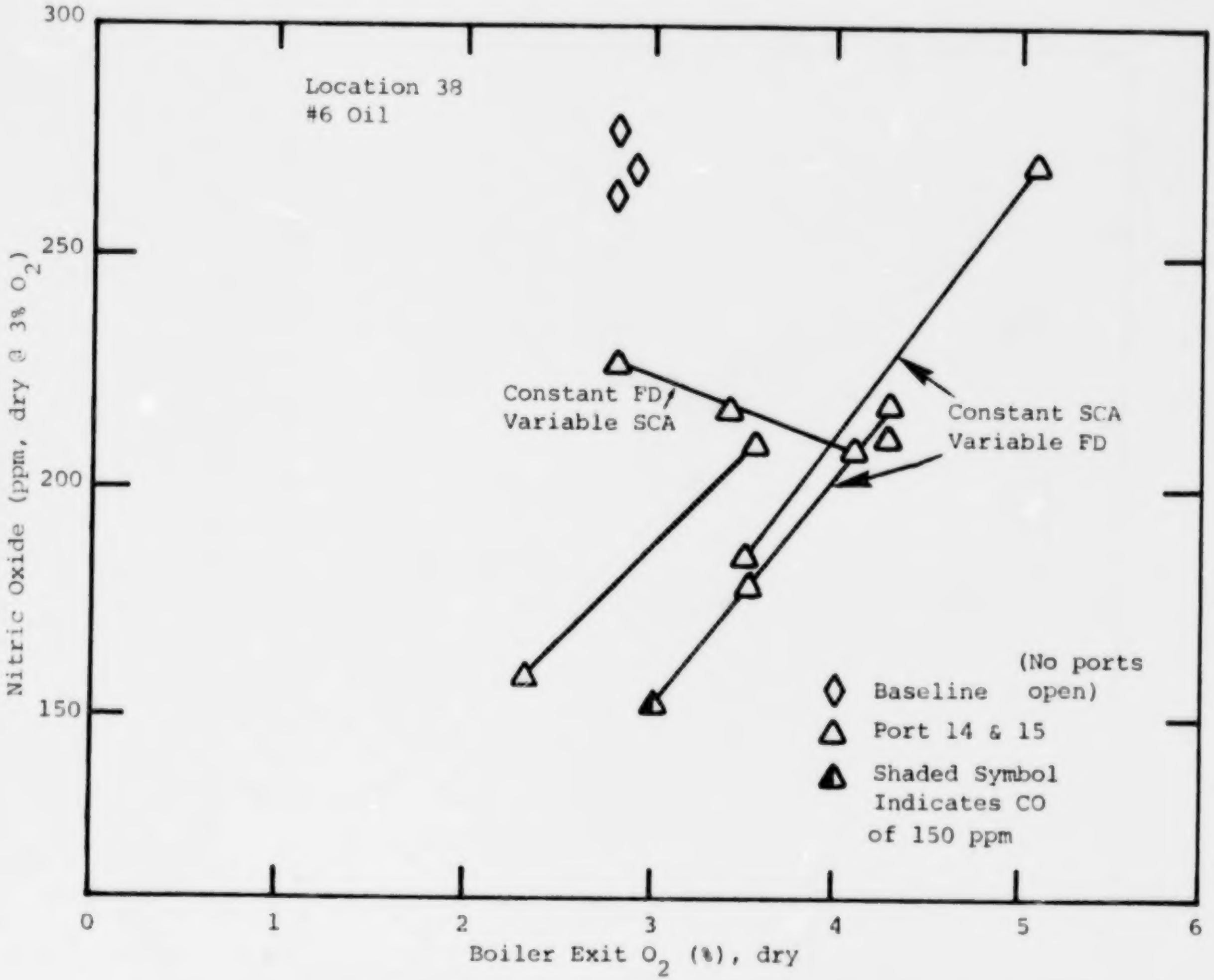

Figure 3-29. Variable SCA - NO_c versus O_2.

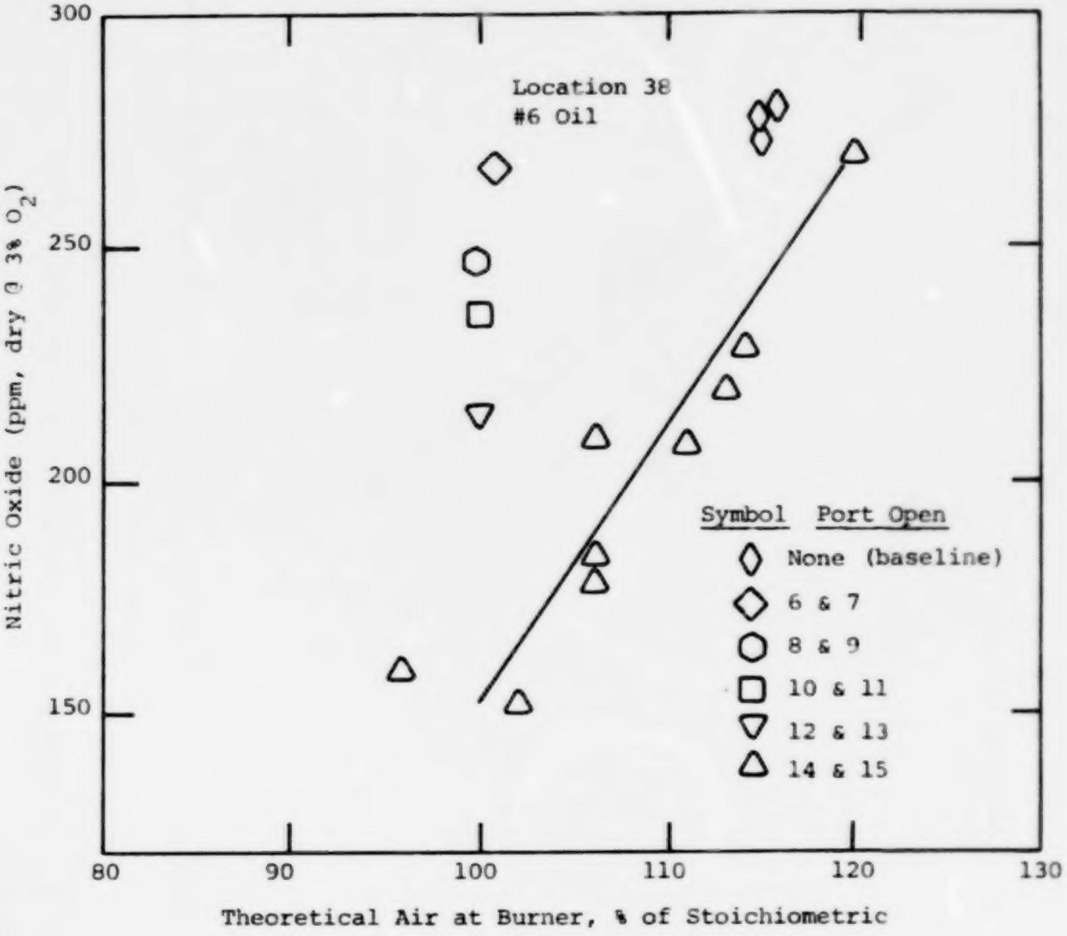

Figure 3-30. SCA single port variations.

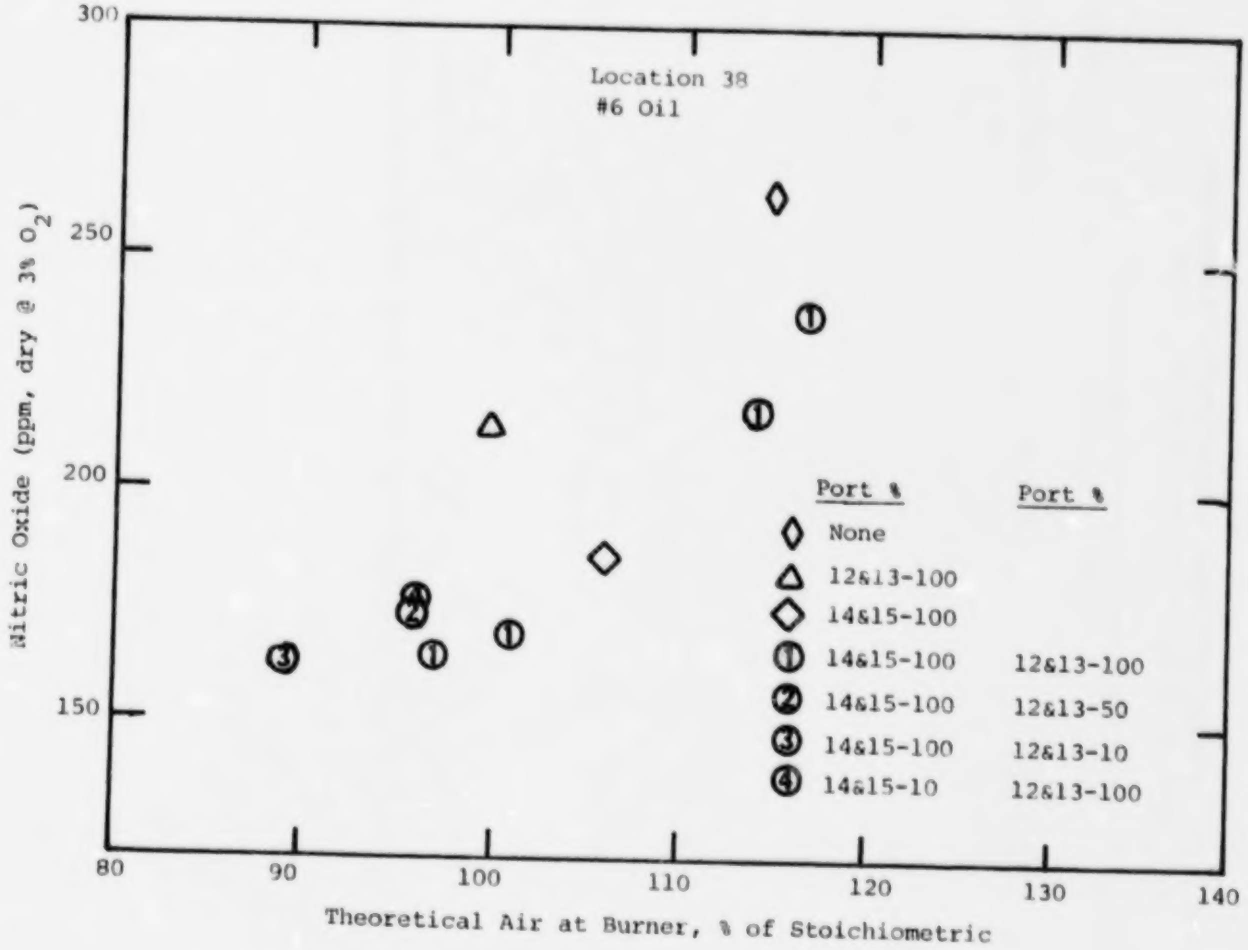

Figure 3-31. SCA single and multiple port variations.

TABLE 3-26. SUMMARY OF METHOD 5 PARTICULATE MEASUREMENTS FOR LOCATION 38 STEAM BOILER FIRING NO. 6 OIL

Condition	Test No.	Total Particulate ng/J (lb/MMBtu)	Solid Particulate ng/J (lb/MMBtu)
Baseline	200-24	66.4 (0.154)	36.6 (0.085)
Low Excess Air	201-12	47.6 (0.110)	38.3 (0.088)
	201-15	43.7 (0.101)	38.7 (0.089)
Staged Combustion Air	203-26A	52.6 (0.122)	38.7 (0.900)
	203-26B	62.2 (0.144)	39.9 (0.920)
Variable Air Preheat (Min. Temperature)	202-4	54.4 (0.126)	37.6 (0.087)

TABLE 3-27. SO_x SUMMARY, LOCATION 38 FIRING NO. 6 OIL

	O_2		SO_2	SO_3
	Boiler Exit	Stack	ppm-Corrected to 3% O_2	
Baseline				
200-23	2.9	6.8	944	28
Low O_2				
201-12*	1.55	5.7	948	13.5
201-14*	1.5		1000	35.9
			Avg. 974	Avg. 25
SCA				
203-26*	3.1	7.72	1010	14.0
203-27	3.4	7.1	968	13.9
			Avg. 989	Avg. 14

*Single sample

indicate that the level of total sulfur oxides emissions is dependent only upon the fuel sulfur content and not upon operating mode. The data indicate that staged combustion air resulted in a 50% reduction in SO_3.

The particulate size distribution for boiler operation with #6 fuel oil is presented in Figure 3-32 for four operating modes. Particle size diameter is plotted as a function of cumulative proportion of the impactor catch for baseline, staged combustion air, low O_2 and variable preheat operation. The data indicate that the particle distribution is not represented by a log-normal distribution since the data do not plot as a straight line. The cumulative proportion of impactor catch below 3 μm diameter varied from 65 to 94%, indicating that the particulate catch for all operating modes is of very small diameter material. For all operating modes, between 60 and 88% of the catch is below 1 μm diameter. All combustion modifications resulted in increased particle size, compared with baseline. Low excess O_2 operation produced the largest particle size with only 65% of the particulate below 3 μm.

3.2.4 Combustion Modifications With Natural Gas

Excess Air Variations--

The NO versus O_2 data for natural gas are presented in Figure 3-33. Baseline measurements show 162 ppm NO at 1.6% O_2. The excess oxygen was varied from a low of 1.25% to a high of 4%. At the low O_2 setting CO values of > 2000 ppm were measured, while NO went to a low of 139 ppm. The unit should not be operated at this low O_2 level. High CO firing caused efficiency loss and was a dangerous operating mode. Increasing O_2 to approximately 1.5% decreased CO to approximately 300 ppm. The NO peaked at 175 ppm for approximately 3% O_2.

Variable Preheat (VPH)--

The data for variable preheat temperature with natural gas fuel show a big decrease in NO with reduced windbox temperature (Fig. 3-34). Dropping windbox temperature from a baseline condition of 284 °F to a low of 145 °F

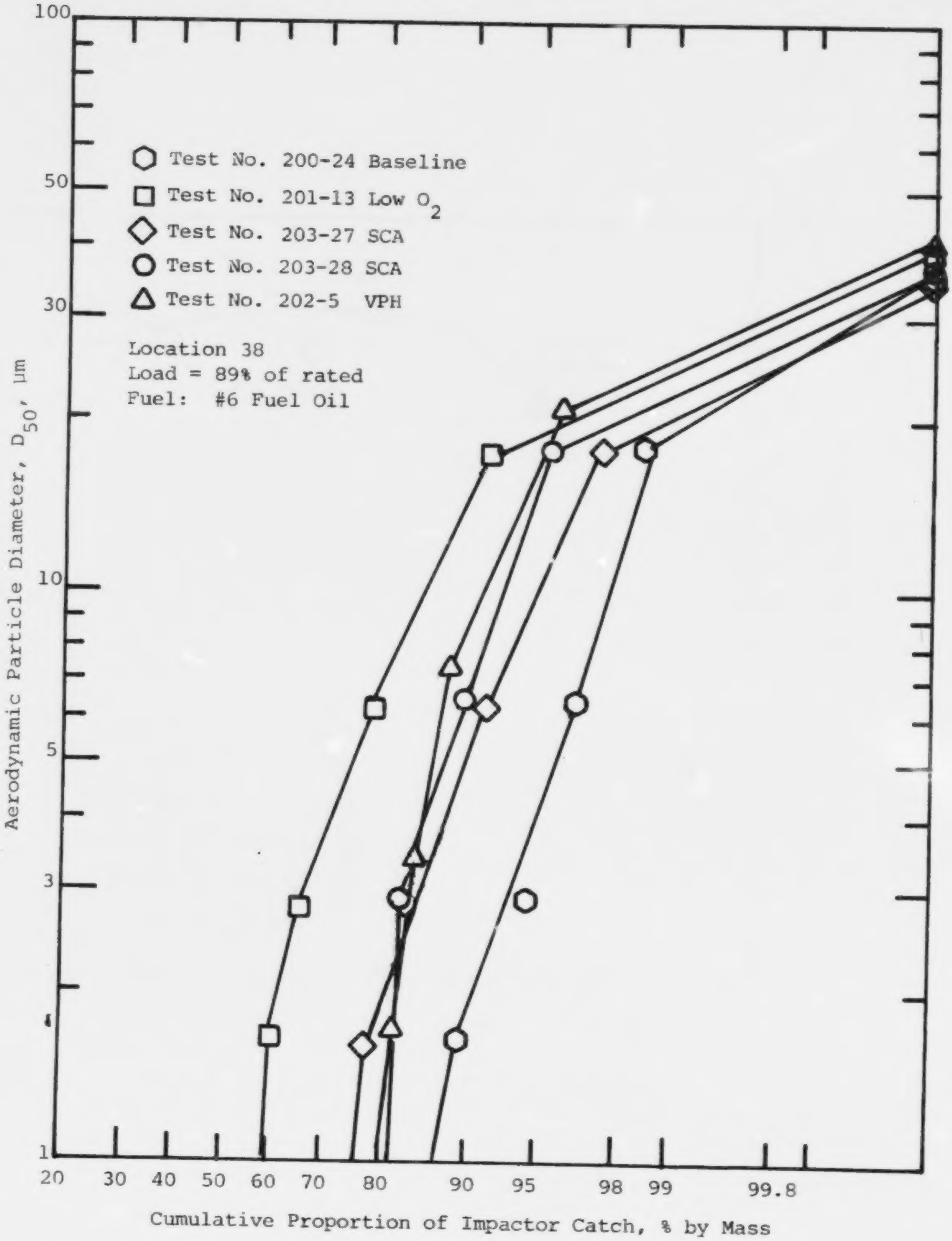

Figure 3-32. Particulate size distribution for an oil fired steam boiler.

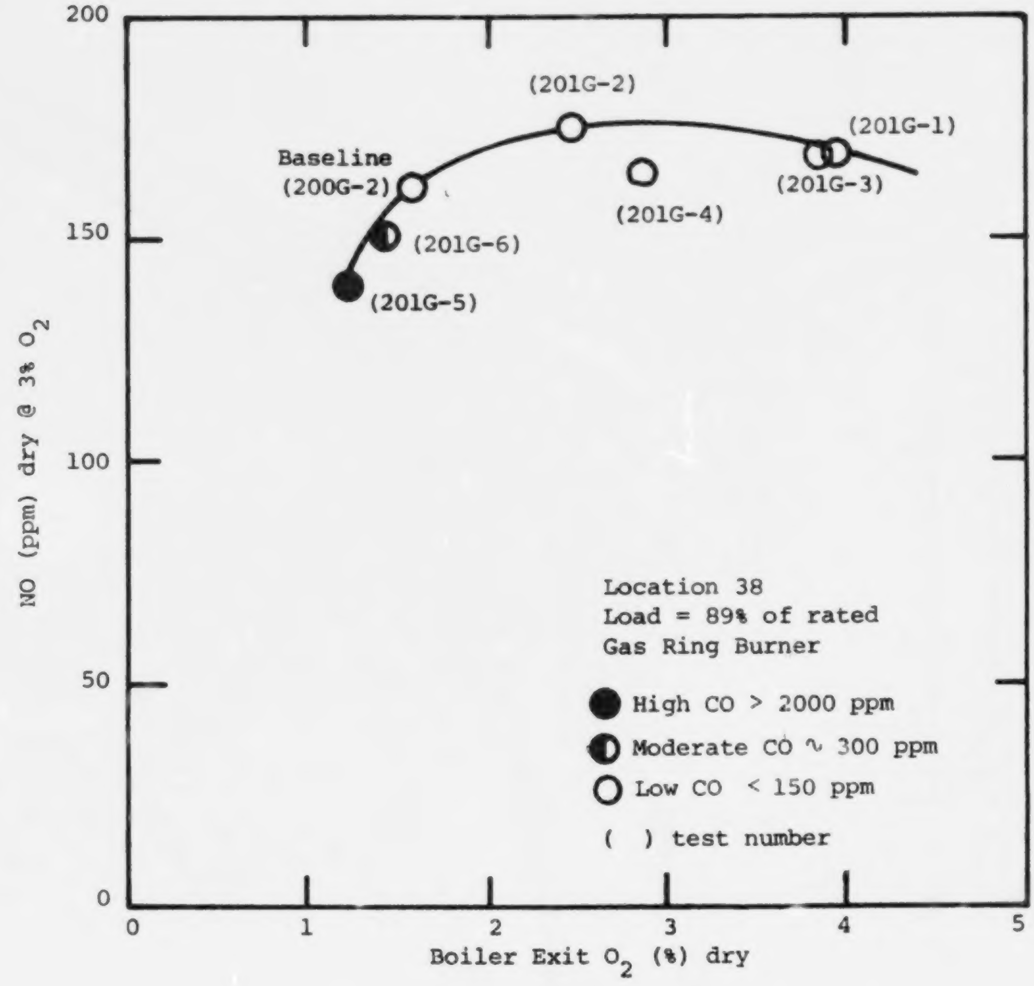

Figure 3-33. The effect of excess oxygen on NO emissions (natural gas).

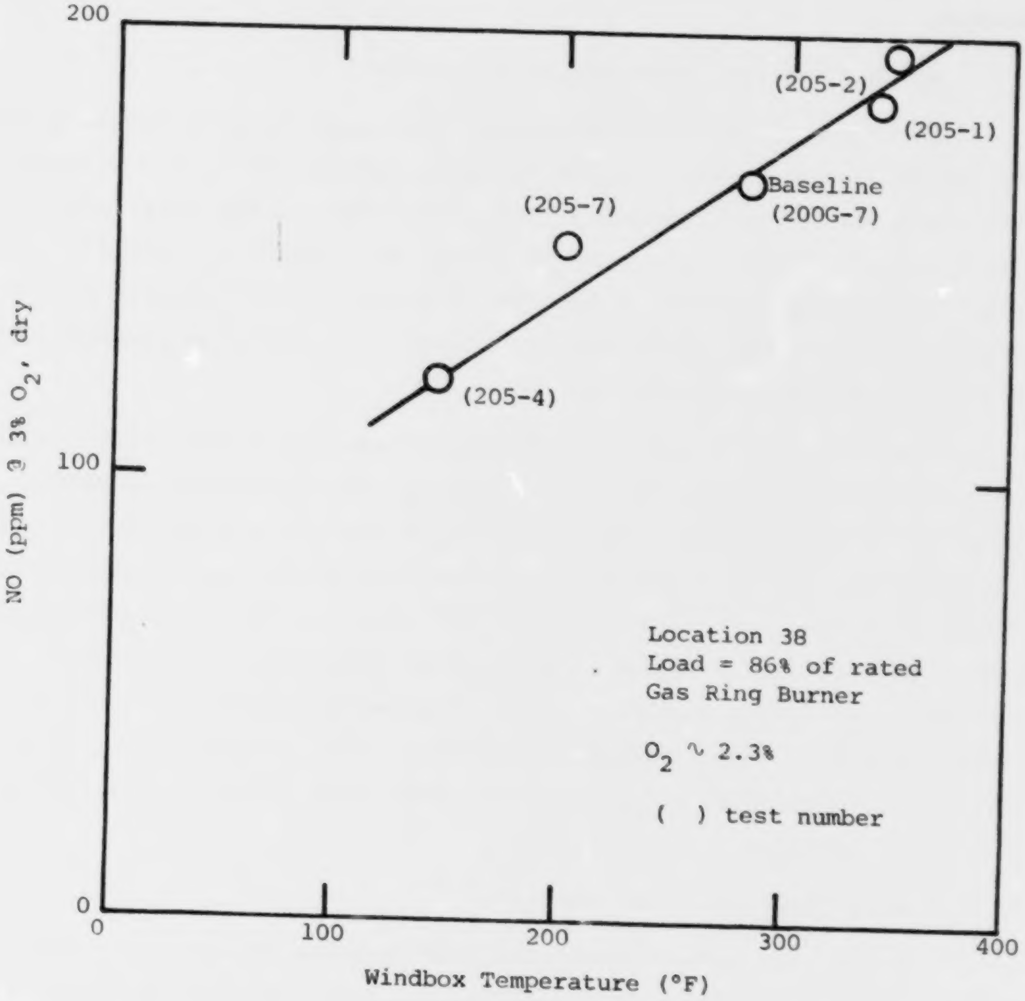

Figure 3-34. The effect of windbox temperature on NO emissions (natural gas).

reduced NO emissions from 166 ppm to 122 ppm. All tests in this series were conducted at a load of 86% of rated load with an excess oxygen level of approximately 2.3%. The NO decreased by 3.65 ppm/10 °F windbox temperature reduction.

Windbox Register Vane Setting Variation--

Variation of the windbox register vane angle testing was performed with natural gas and shows that NO increases significantly as the vanes which swirl the air entering the burner throat were closed (Fig. 3-35). The increased swirl contributed to better mixing and results in higher NO emissions. Closing the register vanes also decreased the effective area for air entering the burner which increased the FD fan discharge pressure and reduced the maximum obtainable air flow.

The FD fan was required to operate at maximum output for register settings of 54 degrees and less. The nominal baseline operating vanes setting is 66 degrees open. Even with the FD fans at maximum it was necessary to increase the furnace draft to obtain sufficient air flow to prevent CO. To maintain proper operating O_2 levels (approximately 2.4%), high negative furnace pressures are required. The lower NO observed at the 42 degree vane position required 0.6 in. H_2O negative furnace draft (compared to -0.2 in. H_2O) which would raise the furnace leakage considerably. Thus, the actual burner excess air is probably lower than would be indicated by the measured 2.5% O_2.

Staged Combustion Air (SCA)--

The data for staged combustion port location versus NO for natural gas (Fig. 3-36) shows again as it did for oil fuel, that the most effective location for staged air are the ports 14 and 15. In addition, ports 6 and 7, those nearest the burner, exhibited the same effectiveness on NO reduction as did the previously mentioned ports 14 and 15.

The differences seen with natural gas may result from: (1) the different geometric relationship between the burner fuel and air flows with the two fuels (the oil gun being in the center of the burner air flow and the gas ring being on the outside of the burner air flow and more directly influenced by the secondary air), and (2) the greater sensitivity of the NO emissions to combustion air temperature with natural gas.

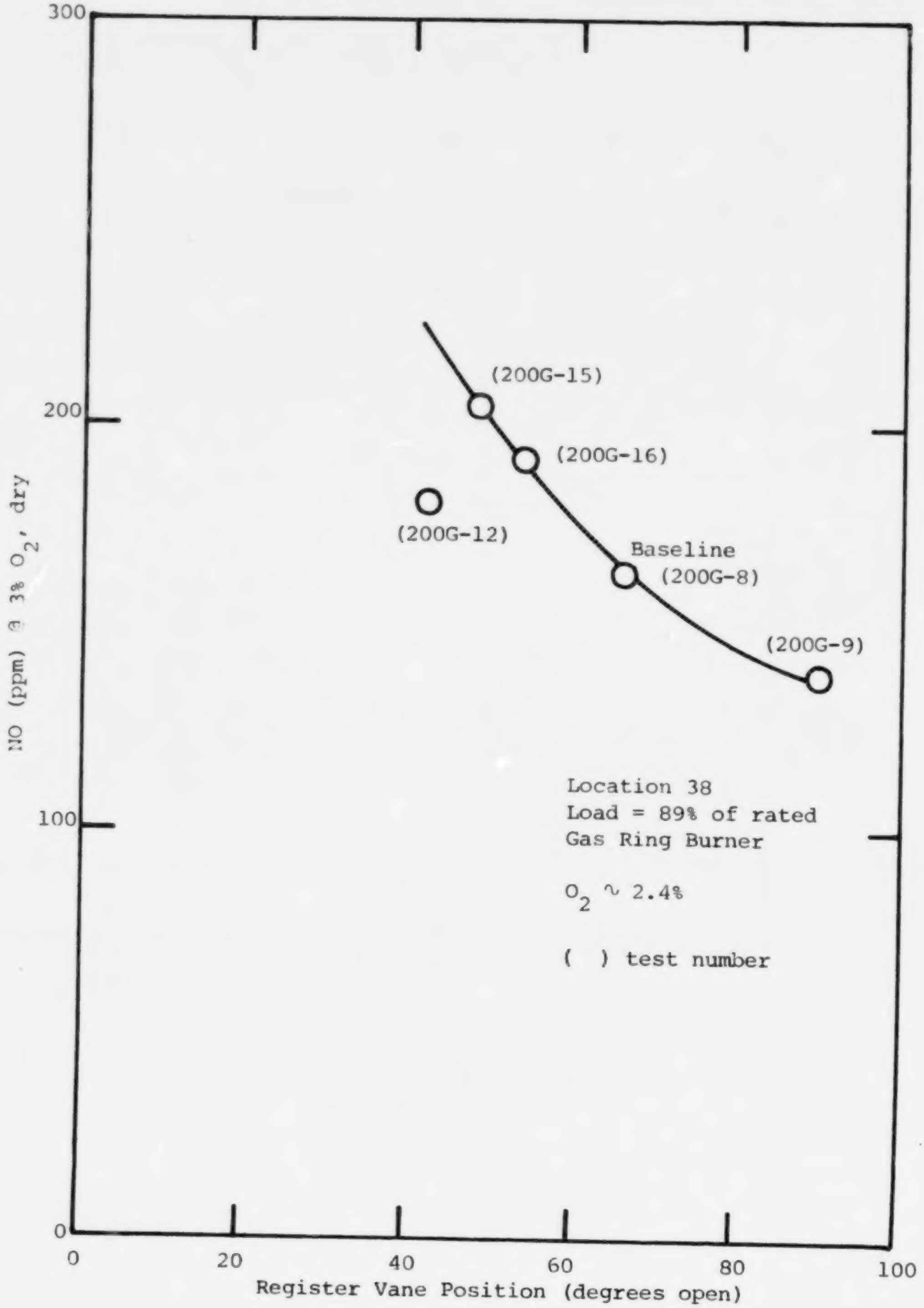

Figure 3-35. NO versus windbox register setting (natural gas).

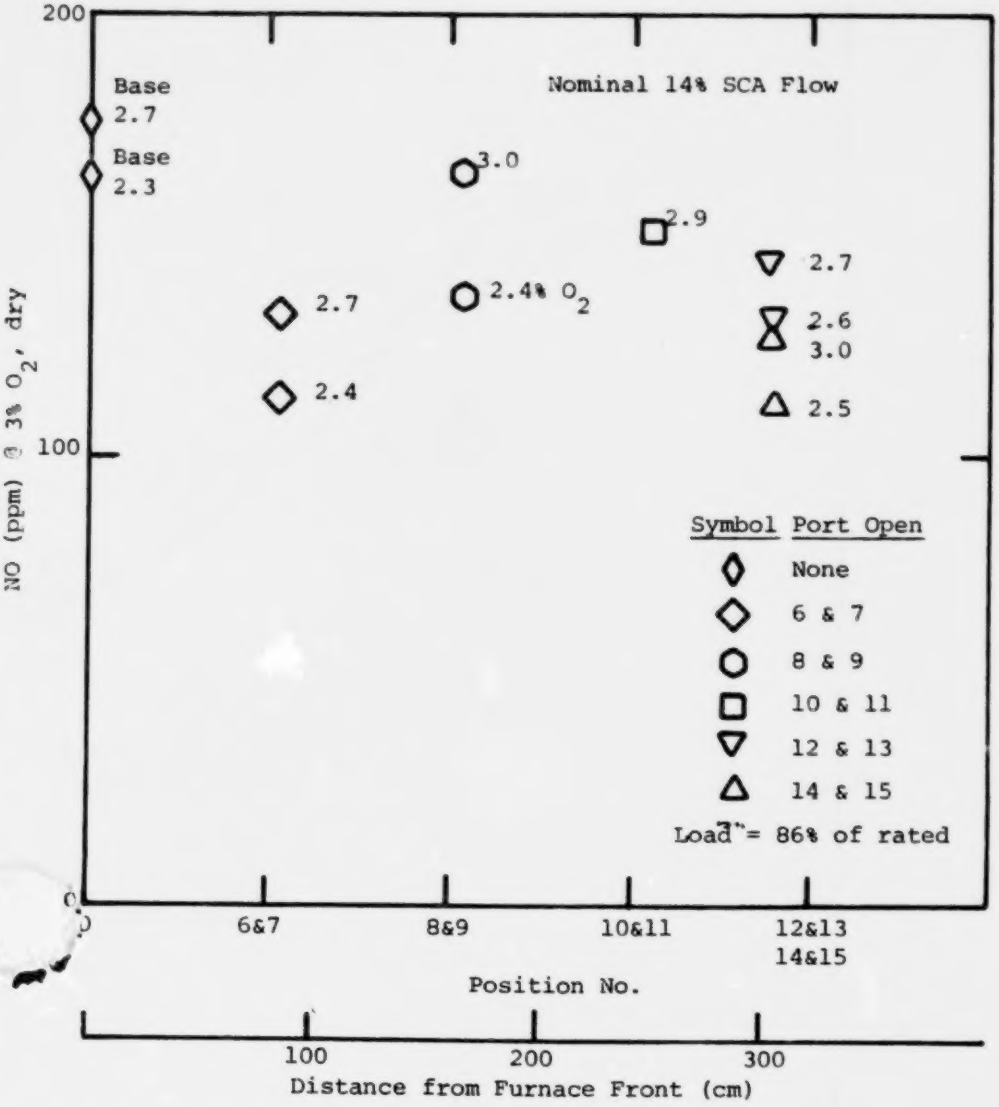

Figure 3-36. NO versus SCA - port location for natural gas fuel.

Figure 3-37 shows the effect of variable SCA fan and FD fan versus NO and O_2 for natural gas fuel. The lowest NO levels correspond to the minimum burner air flows. NO data as a function of the percent of stoichiometric air at the burner are presented in Figure 3-38. These data demonstrate the dominance of burner stoichiometry over total boiler stoichiometry in regard to NO emissions.

The operation on natural gas using single and multiple port locations combined with full air heater bypass (Fig. 3-39) indicates that very low values of NO can be obtained. An NO reduction of 69% relative to the baseline condition was measured. The three best SCA port locations indicated little difference in NO emissions with ports 6 and 7 and 14 and 15 being slightly better than ports 12 and 13. All three port locations indicate some CO emissions with ports 12 and 13 and 6 and 7 showing 200-400 ppm. The full open bypass requires maximum ID fan capacity to maintain 0.5 kPa (0.2 in. H_2O) negative furnace pressure with one pair of ports open and operated at negative pressures near 0.25 kPa (0.1 in. H_2O) with 2 pairs of SCA ports fully open.

3.2.5 Boiler Thermal Efficiency

Boiler thermal efficiency was calculated based on the ASME Heat Loss Method for various operating modes. The calculated efficiency as a function of boiler operating condition for both natural gas and #6 oil was presented in Table 3-23.

Very little effect of operating mode on efficiency was exhibited with both natural gas and #6 oil. With natural gas, a slight increase in efficiency was shown with lowered excess O_2 and the variable preheat test showed a loss in efficiency of 1%. With #6 oil, the low O_2 condition resulted in slightly higher efficiency (0.8%) than the baseline condition but the variable preheat test showed nearly a 3% degradation in efficiency.

3.2.6 Conclusions From Location 38 Tests

The tests conducted on the watertube boiler at Location 38 permitted an evaluation of several combustion modification techniques using #6 oil and natural gas fuel. The following combustion modifications were evaluated: lowered excess air, variable preheat temperature, staged combustion air

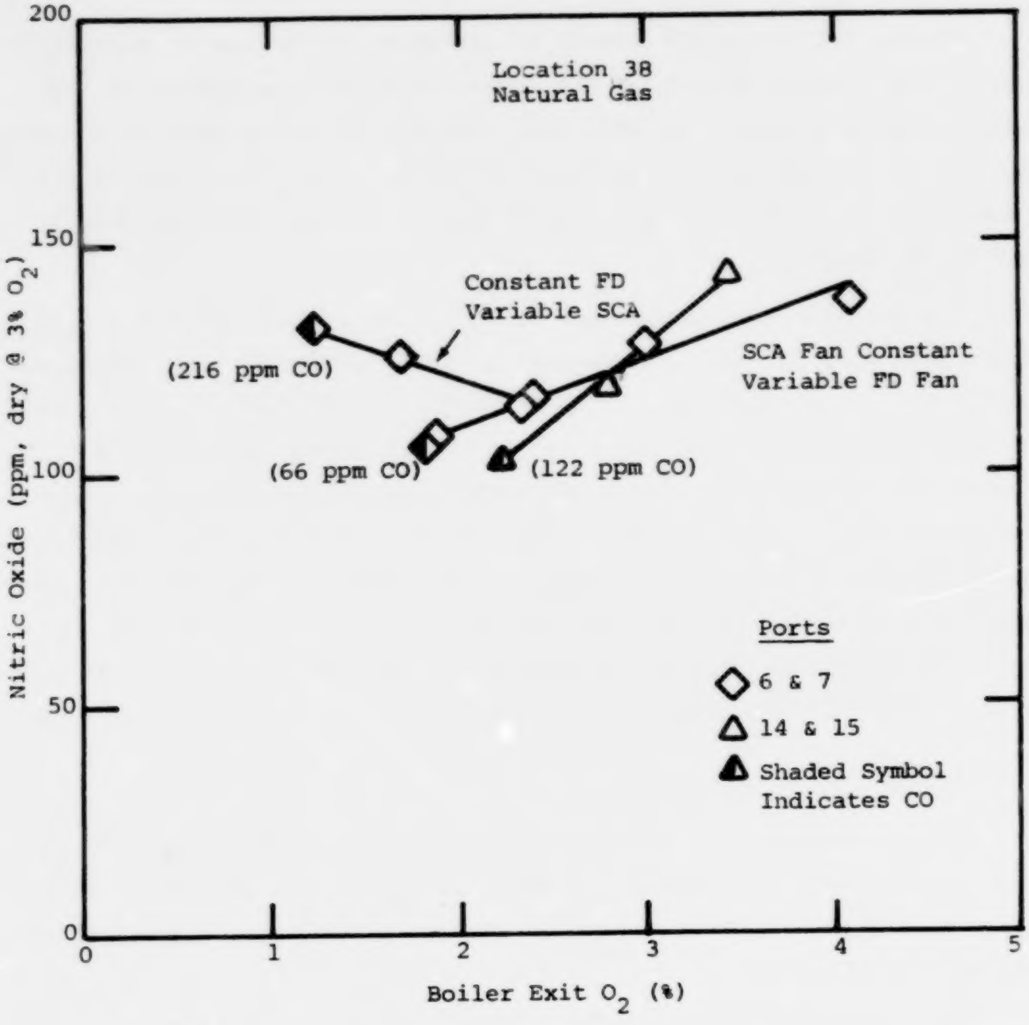

Figure 3-37. Variable SCA - NO_c versus O_2

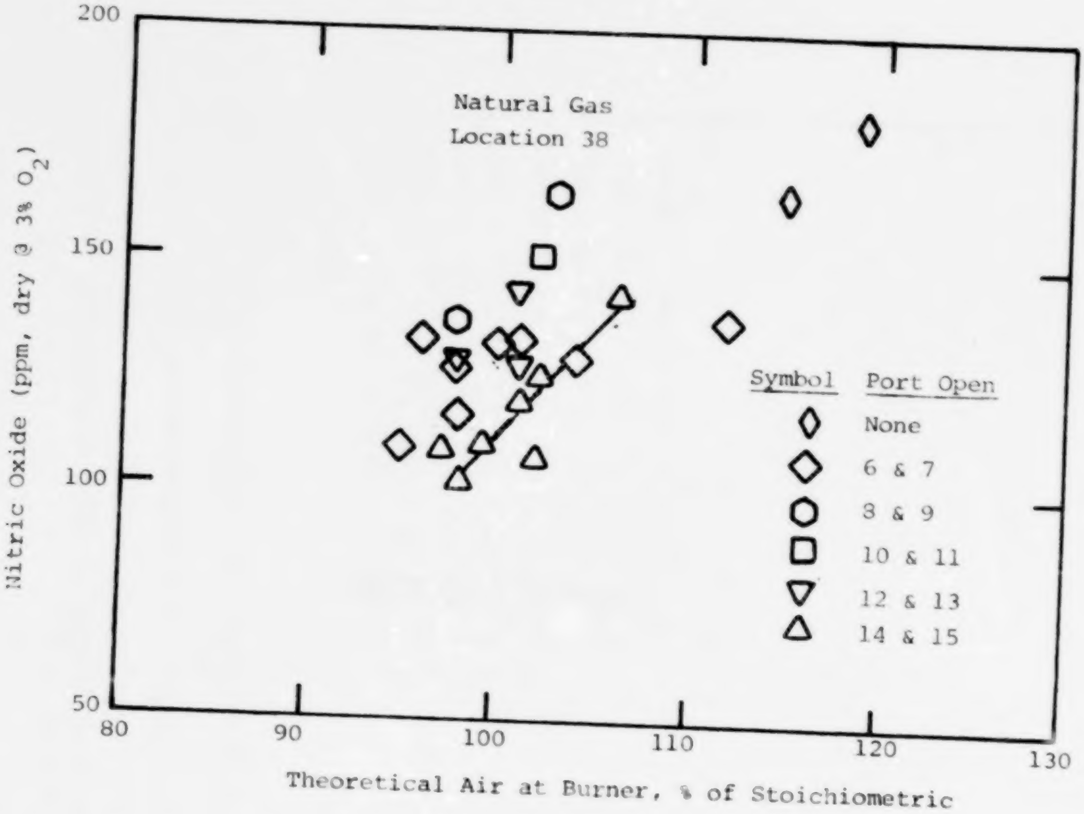

Figure 3-38. SCA single port, Tests 204-1 through 204-22.

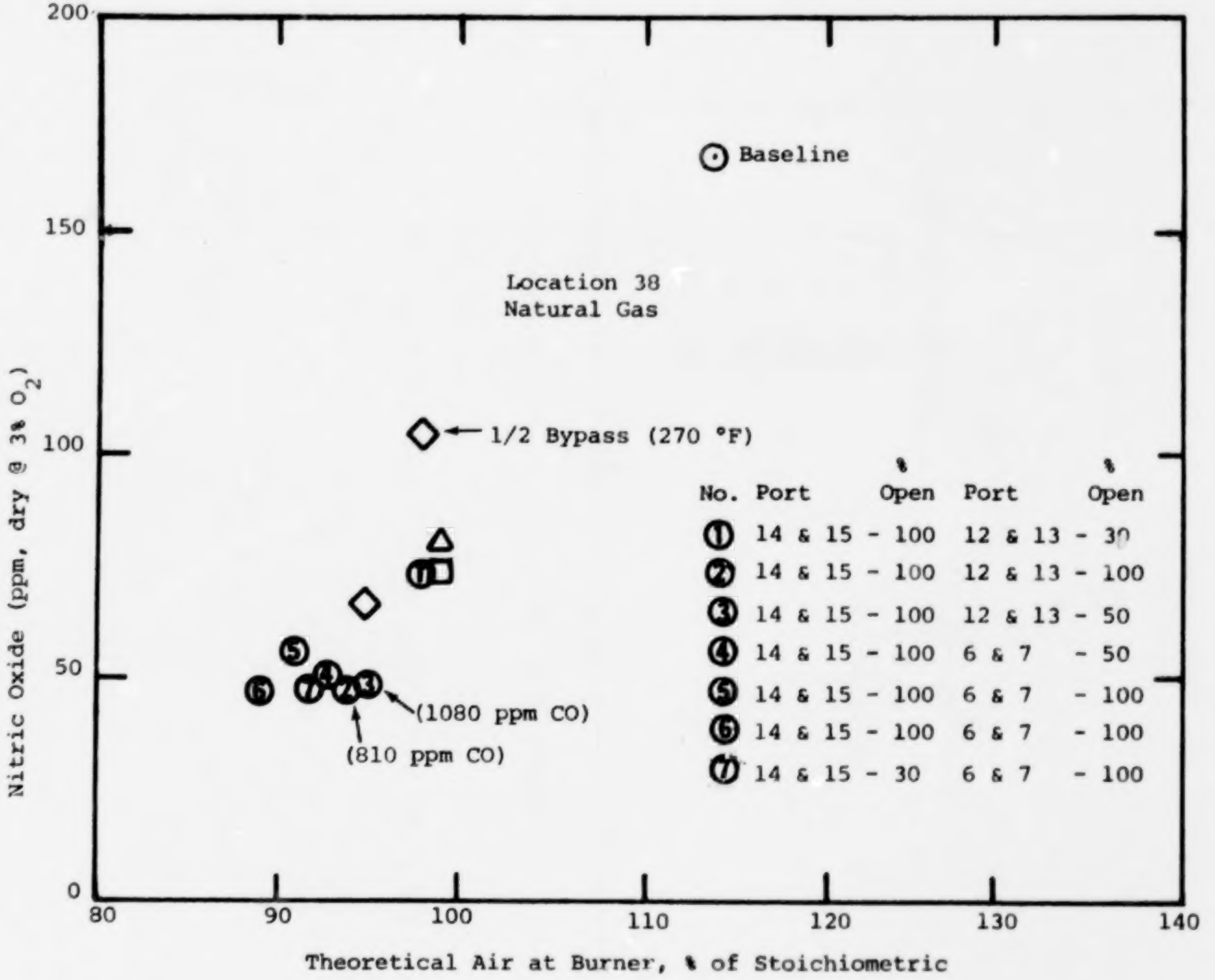

Figure 3-39. SCA multiple port combinations with air heater bypass 100% (∿ 140 °F), Tests 204-23 through 204-32.

injection at different port locations, windbox register vane setting variations and combinations of these. The data previously presented in Table 1-5 show the reduction in NO from the baseline condition as a function of combustion modification and type of fuel. The data show that the maximum reduction in NOx while firing natural gas was accomplished with a combination of staged combustion and lowering the air preheat temperature. This combination resulted in a 69% reduction in NO_x from the baseline condition. While firing #6 oil, the maximum reduction demonstrated was 43% using staged combustion air and lowered excess O_2.

The excess O_2 data indicate that the effect of O_2 on NO for natural gas is leveling off above approximately 2-1/2% O_2. The maximum reduction, at 1.25% O_2, was approximately 14% less than the nominal condition. With #6 oil a similar trend was exhibited. The reduction was approximately 20% from the nominal condition of 2.9% O_2.

The reduction of windbox air temperature showed a large decrease in NO emissions for both fuels. The windbox temperature variation had a greater effect on NO with natural gas firing than with #6 oil firing. Nominal values of NO decreases were 3.65 ppm/10 °F for natural gas and 2.75 ppm/10 °F for #6 oil. These NO reductions were accompanied by a loss in thermal efficiency. With natural gas there was a decrease of 2 points in efficiency when air temperature was lowered to 145 °F, and with #6 oil there was a loss of 3 points when air temperature was lowered to 128 °F. Baseline air temperatures were 283 and 272 °F for natural gas and #6 oil, respectively.

The data for NO versus SCA port location for oil fuel indicate, that the most effective injection point is the most distant from the burner. The data for natural gas firing indicate a similar trend, except that the ports nearest the burner exhibited the same effectiveness as did the most distant ports. This may be due to the different geometric relationship between burner fuel and air flows (center oil gun versus outside ring gas burner) and greater sensitivity of the NO emissions to combustion air temperature with natural gas. At the nominal condition of 2.8% O_2 and 14% SCA flow, the NO_x was reduced 30% for #6 oil with injection at approximately 300 cm from the furnace front. Reducing the operating O_2 to 2.3% reduced the NO_x by 42% from the baseline condition. Staged combustion with natural gas resulted in a reduction of 32% from the baseline condition with the boiler operating at 2.4% excess O_2 and 14% SCA.

Windbox register adjustment reduced NO on natural gas fuel by 18% from the baseline condition. For natural gas the maximum reduction occurs with the combination of air preheater bypass and SCA multiple port combination. Test 204/5-30 shows a 69% NO reduction, with no apparent side effects.

REFERENCES

1. Cato, G. A., et al., "Field Testing: Application of Combustion Modifications to Control Pollutant Emissions from Industrial Boilers - Phase I," EPA 650/2-74-078a, NTIS Order No. PB 238 920, June 1975.

2. Cato, G. A., et al., "Field Testing: Application of Combustion Modifications to Control Emissions from Industrial Boilers - Phase II," EPA 600/2-76-086a, NTIS Order No. PB 253 500, April 1976.

3. Hamersma, J. W., Reynolds, S. L., and Maddalone, R. F., "IERL-RTP Procedures Manual: Level I Environmental Assessment," EPA Report 600/2-76-160a, NTIS Order No. PB 257 850, June 1976.

APPENDIX A

TRACE SPECIES AND ORGANICS SAMPLING AND ANALYSIS PROCEDURES

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Note: Units on values in this Appendix are given in the actual English or metric units as used or measured on field equipment. Alternate English to metric, or metric to English conversions are not listed to avoid confusion, as the Appendix is intended for direct field use.

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A-1.0 INTRODUCTION

Sampling and analysis procedures for trace species and organics emissions used in the current program were based on procedures developed by the EPA Industrial Environmental Research Laboratory at Research Triangle Park, NC. The IERL-RTP procedures are defined in a procedures manual prepared for EPA by TRW Systems Group (Ref. A-1) that relates the procedures in terms of a multi-media Level I stream prioritization sampling and a Level II detailed assessment sampling. Although those basic sampling procedures were adapted for the current program (with modifications noted herein), this program was not formulated in the specific Level I-Level II framework. Level I sampling is intended to show the presence or absence and, within a factor of ± 2 to 3, the emission rates of all inorganic elements, selected inorganic anions and classes of organic compounds. The current program objective is to obtain qualitative and quantitative data for a large number of elements (approximately 60) by use of spark source mass spectrometry and this objective is similar to the Level I philosophy. A second objective of the current program, more related to the Level II definition, is to more accurately quantify the emissions of the elements, species, and organics as shown in Table A-1, and to relate the emissions of these species, by mass balance, to the amounts input with fuel or process materials. In addition to total quantities, information is required on the relationship of particulate species emissions to particulate size.

The referenced Level I procedures manual refers to several multi-media sampling procedures. The current program is more narrowly concentrated on exhaust emissions from the stacks of industrial combustion devices. Therefore Chapter III "Gaseous Streams Containing Particulate Matter" of the referenced manual is that portion pertinent to the current program. That chapter discusses sampling with the use of a "Source Assessment Sampling System" (SASS). The features of that

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TABLE A-1. TRACE SPECIES AND ORGANICS TO BE IDENTIFIED

Elements

Antimony
Arsenic
Barium
Beryllium
Cadmium
Calcium
Chlorine
Chromium
Cobalt
Copper
Fluorine
Iron
Lead
Manganese
Mercury
Nickel
Selenium
Tellurium
Tin
Titanium
Vanadium
Zinc

Species

Total sulfates
Total nitrates

Organics

Total polychlorinated biphenyls (PCB)
Total polycyclic organic matter (POM)
Specific POM compounds:
- 7, 12 - dimethylbenz (a) anthracene
- Dibenz (a,h) anthracene
- Benzo (c) phenanthrene
- 3-Methylcholanthrene
- Benzo (a) pyrene
- Dibenzo (a,h) pyrene
- Dibenzo (a,i) pyrene
- Dibenzo (c,g) carbazole

sampling train are presented in the referenced manual and will not be repeated here. The remainder of this appendix presents the specifics of the referenced procedures as adopted or modified for the current program.

The SASS sampling train and samples obtained are shown schematically in Figure A-1. The sample combinations for analysis are somewhat different than for Level I.

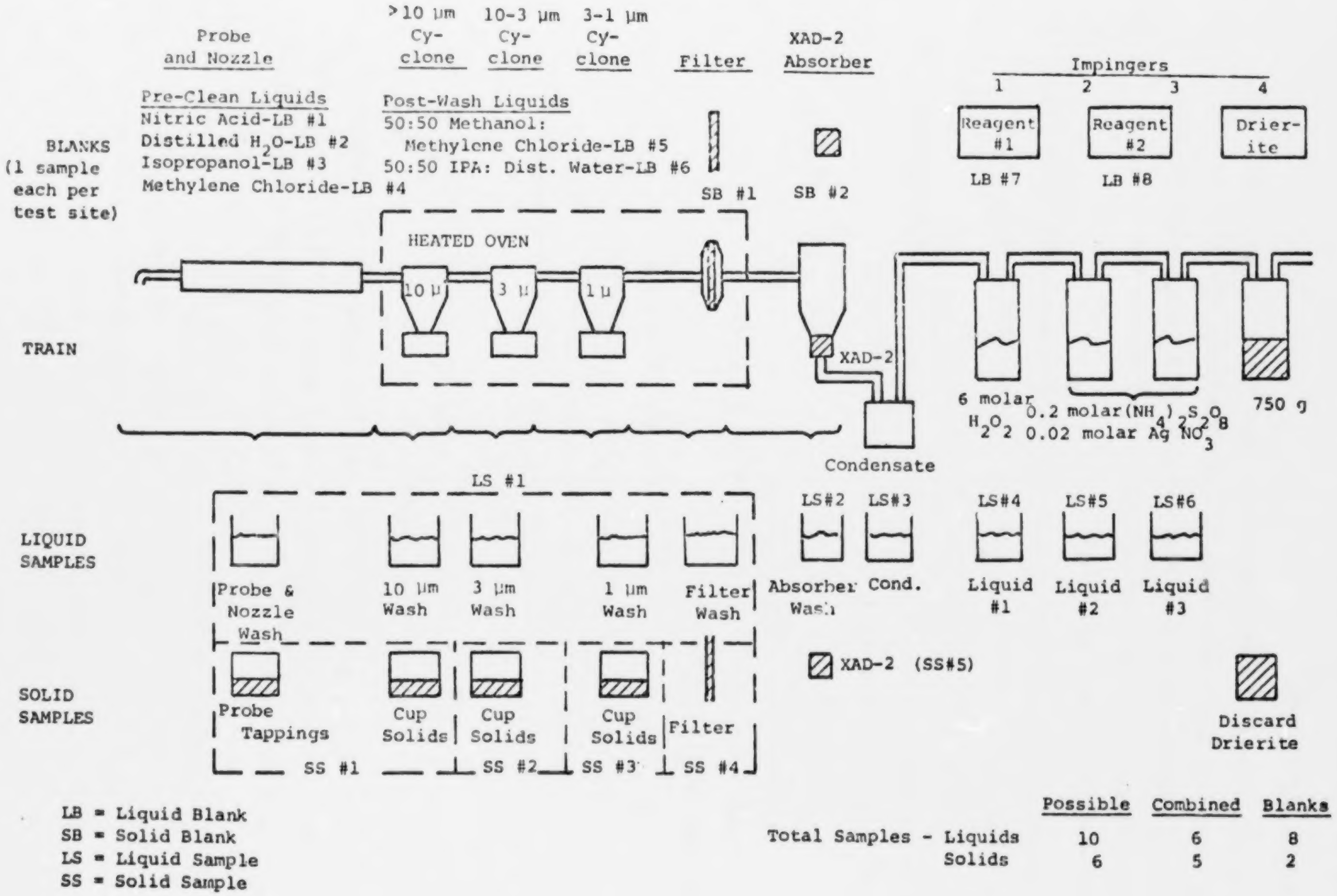


Figure A-1. SASS train schematic.

A-2.0 PREPARATION OF XAD-2 RESIN

A-2.1 General Procedure

The XAD-2 resin to be used in the SASS train sorbent trap must be cleaned prior to use. The resin as obtained from the supplier is soaked with an aqueous salt solution. This salt solution plus residual monomer and other trace organics must be removed before the resin can be used for sampling trace organics.

Clean-up is normally achieved in a giant Soxhlet extractor. Any other continuous extractor working on the same principle of circulating distilled solvent would be adequate.

The wet XAD-2 resin is charged into the extractor thimble and extracted in sequence with refluxing solvent as follows:

1. Water, 20-24 hours
2. Methanol, 20-24 hours
3. Anhydrous ether, 8 hours (during day only)
4. Pentane, 20-24 hours

Methanol is used primarily to remove the water from the resin. Ether removes a substantial portion of the organics--overnight reflux is acceptable if apparatus is secure to the hazards of ether. Pentane is used as the final stage because it is the solvent used to extract the resin after sample collection.

A commercial giant extractor has a dumping volume of 1500 ml and thus about 2.5 l of solvent is required in a 3 l flask.

After the final pentane extraction, the resin is transferred to a clean flask and dried under vacuum aided by mild heat from a heat lamp. Care should be taken (traps) to prevent backstreaming from vacuum systems.

A-2.2 Soxhlet Cleaning of XAD-2

Follow the general procedure given above. However, the following procedural details may be helpful to those not familiar with operating the Soxhlet extractors. These recommendations and comments are based on our recent experience in preparing XAD-2 for EPA SASS tests.

1. Quality of solvents*

   Water: Arrowhead distilled
   Methanol: Anhydrous methyl alcohol, Mallinckrodt, AR grade
   Anhydrous ether: anhydrous (ethyl) ether, Mallinckrodt, AR grade
   Pentane: Mallinckrodt, spectr. AR grade

2. The use of paper (cellulose) thimbles was recommended by ADL. With a soft lead pencil, mark on the outside of the thimble the desired fill line which corresponds to the entrance level of the syphon tube when the thimble is inserted into the extractor. Handle the thimble with plastic gloves. (Glass thimbles are now used in Level I.)

3. Fill (i.e., "charge") the thimble with XAD-2 using a stainless steel spoon. Intermittently moisten the XAD-2 with distilled water (from a plastic wash bottle) to compact the XAD-2 in the thimble. Excess water will flow through the walls of the thimble. In this manner, add XAD-2 up to the pencil fill line.

**4. Install the charged thimble in the extractor, place approximately 300 ml of distilled water in the Soxhlet flask and assemble the Soxhlet extractor. Room temperature tap water is adequate for the condenser cooling.

   When inserting the charged thimble into the Soxhlet, make a small indent at the bottom of the thimble to avoid obstructing the inlet to the syphon tube.

5. Bring the water to a boil and allow the extractor to syphon several times (one hour of operation is adequate). Discard the flask contents, refill with fresh distilled water and continue the extraction. By discarding the initial water, most of the salt originally contained in the raw XAD-2 is removed from the system. This will prevent salt carryover back into the XAD-2 and will "even out" the boiling.

6. The methanol solvent should also be replaced in a similar fashion. This assures complete removal of the water. (Any water remaining during the ether extraction stage will "plug" the XAD-2 pores thereby interferring with the ether extraction.) Three hundred to four hundred ml of methanol in the extraction flask is adequate for all-night operation. Use room temperature tap water for the condenser.

*Mention of trade names does not constitute approval by U.S. EPA.
**Soxhlets actually used were not the giant type.

7. For the ether and pentane extraction, a circulating ice bath should be used for condenser cooling to minimize vapor loss through the top of the condenser. Three hundred to four hundred ml of solvent is adequate for all-night pentane operation. To avoid condensing water (from the air) on the inside of the condenser during startup, operate the Soxhlet for several minutes without condenser cooling (until solvent vapors purge out the air) before turning on the circulating water.

8. Use extreme caution when handling ether and pentane. Both are extremely volatile and highly flammable. Make sure all heating mantles, electrical equipment, etc. are off while containers are open.

9. The Soxhlet reflux rate can be judged by observing the drip rate from the condenser onto the XAD-2. One to Two drops per second is desirable. This is accomplished by adjusting the power to the heating mantle. For this condition, the water may be boiled vigorously but no boiling (bubbling) will be observed for the other three solvents.

10. When changing over from one solvent to another, residual solvent remaining in the thimble and extractor should be removed to as high degree as practical(i.e., do not desiccate or vacuum dry). One approach which works quite well is to apply suction to the discharge end of the Soxhlet syphon tube. The use of a plastic "filtering pump" (an aspirator pump operated by tap water from the faucet) has proved adequate.

11. While drying the XAD-2 in the vacuum desiccator, heat to approximately 120°F using heating lamps. Do not use vacuum grease on the desiccator. Protect the vacuum pump from pentane vapors with a carbon trap. The XAD-2 may be left in the paper thimbles while drying in the desiccator. Use a filter (i.e., cotton in a flask) between the carbon trap and the desiccator to prevent backflow of carbon into the XAD-2 in the event of a rapid loss of desiccator vacuum.

A-3.0 PREPARATION FOR A SAMPLING RUN

A-3.1 Containers, Chemicals, and Laboratory Equipment

Table A-2 lists the samples to be recovered from the SASS train and the recommended containers used for sample storage and shipping. In some cases more than one container may be required. All containers should be cleaned prior to use according to the procedure used for cleaning the train as described in Section A-2.2.

Laboratory Equipment--

All sample recovery operations, sample weighing, and chemical cleaning of train components and containers should be performed in a clean area specially set aside for this work. In the field, this "clean room" should consist of at least a clean enclosed work bench or table top and every attempt should be made to observe the following general recommendations:

1. Avoid drafts and areas with high foot traffic
2. Keep floors swept to minimize air borne dust
3. Use plastic table cloths
4. Inlet filters on air conditioners should be in place
5. Use common sense to avoid contaminating samples with hair, fingerprints, perspiration, cigarette smoke or ashes, etc.
6. Use plastic gloves or forceps when handling tared containers; stainless steel tweezers when handling filters

In addition to sample containers listed in Table A-2, the following clean room accessories will be required:

SASS train tool kit
stainless steel tweezers (2)
stainless steel spatulas (2)
disposable plastic gloves
teflon or "guth" unitized wash bottles (3)
teflon policeman (optional)
110°C drying oven
weighing balance 160 gram capacity required
assorted powder and liquid funnels
assorted graduated cylinders, 250 ml to 1000 ml
1/2-gal mixing jugs (3)

TABLE A-2. SAMPLE STORAGE/SHIPPING CONTAINERS

Train Component	Sample Type	Container Required[*]
Probe and nozzle	solid tappings	Tared 4 oz. LPE[†]
	solvent wash	500 ml amber glass (16 oz)
10μ cyclone	cup solids	Add to probe and nozzle tappings.
	solvent wash	Add to probe and nozzle wash.
3μ cyclone	cup solids	Tared 4 oz. LPE
	solvent wash	500 ml amber glass (16 oz)
1μ cyclone	cup solids	Tared 4 oz. LPE
	solvent wash	500 ml amber glass (16 oz)
Filter holder and filter	solid tappings and filter	Tared 150 mm glass petri dish
	solvent wash	500 ml amber glass (16 oz)
XAD-2 Module:		
(1) XAD-2 resin	solid adsorbent	500 ml amber glass (wide mouth) (16 oz)
(2) Condensate	contents of condensate cup	1 liter LPE
(3) All surfaces	solvent wash	500 ml amber glass (16 oz)
Impinger #1	contents	1 liter LPE, with pressure relief cap
	rinses	500 ml amber glass (16 oz)
Impinger #2	contents	1 liter LPE
	rinses	500 ml amber glass (16 oz)
Impinger #3	contents	1 liter LPE
	rinses	500 ml amber glass (16 oz)

[*] All glass containers must have teflon cap liners.

[†] Linear polyethylene (same as "high density" or "type 3" polyethylene).

Additional sample bottles must be provided for all fuel, process materials, and ashes to be collected. For train washes and liquids, particularly the condensate, several bottles may be required.

Quality of Chemicals--

An underlying concern in selecting chemicals for impinger solution and washes is to avoid introducing trace compounds similar to those being analyzed. Although "blanks" of impinger solutions will be analyzed, it is preferable to minimize chemical impurities when possible by using highest quality chemicals rather than adjust the final sample analyses results. The following chemical grades were used:

Chemical	Quality
Impinger Solution:	
distilled water	Commercial distilled
ammonium per(oxydi)sulfate $[(NH_4)_2S_2O_8]$	AR
0.1 N silver nitrate ($AgNO_3$)	
30% hydrogen peroxide (H_2O_2)	AR
Train Precleaning:	
distilled water	Commercial distilled
isopropyl alcohol $[CH_3CH(OH)CH_3]$	Spectr AR
methylene chloride (CH_2Cl_2)	Spectr AR
Sample Recovery:	
distilled water	commercial distilled
methylene chloride (CH_2Cl_2)	Spectr AR
methanol (CH_3OH)	Spectr AR
isopropyl alcohol $[CH_3CH(OH)CH_3]$	Spectr AR

If higher grade (lower impurity levels) of chemicals are available they should be used.

A-3.2 Cleaning the SASS Train

Newly purchased or previously unused train components and sample containers should be washed with tap water and a plastic scouring pad. All surfaces in the sampling train which come in contact with sample, as well as all sample containers and impingers, should be prepassivated by one-hour standing contact with a 50:50% volume solution of pure nitric acid and distilled water. Remove any remaining traces of acid by rinsing with tap water, then continue with the solvent cleaning procedure below.

Prior to sampling, all SASS train components and sample containers are cleaned in two or three successive stages (in the order listed) using a different solvent in each stage:

All Except Impinger Sample Bottles	Impinger Sample Bottles
1. distilled water	1. distilled water
2. isopropyl alcohol	2 isopropyl alcohol
3. methylene chloride (CH_2Cl_2)	

The distilled water may be dispensed in plastic wash bottles; the isopropyl alcohol and CH_2Cl_2 should be dispensed using teflon or glass wash bottles. After each part is washed with CH_2Cl_2, it should be dried in a filtered stream of dry air or nitrogen.

Any solid residues adhering to the internal surfaces should be removed with tap water and a plastic scouring pad before proceding with the solvent cleaning procedure.

After cleaning, assemble and cap off the cyclone assembly. (All caps should be previously cleaned according to the above 3-solvent procedure.) Cap off other sections of the train including the probe, XAD-2 module, filter housing, impinger trains, and interconnecting hoses.

A-3.3 Impinger Solutions

Impinger	Reagent	Quantity	Purpose
#1	6M H_2O_2	750 ml	Trap reducing gases such as SO_2 to prevent depletion of oxidative capability of trace element collecting impingers 2 and 3
#2	0.2M $(NH_4)_2S_2O_8$ + 0.02M $AgNO_3$	750 ml	Collection of volatile trace elements by oxidative dissolution.
#3	0.2M $(NH_4)_2S_2O_8$ + 0.02M $AgNO_3$	750 ml	Collection of volatile trace elements by oxidative dissolution.
#4	* Drierite (color indicating)	750 g	Prevent moisture from reaching pumps

Suggested Formulas for Preparing Impinger Solutions--

Impinger #1 (6M H_2O_2)

To prepare 750 ml of 6M H_2O_2 dilute 465 ml of standard 30% (by weight) H_2O_2 with distilled water.

Impingers #2 and #3 [0.2M $(NH_4)_2S_2O_8$ + 0.02M $AgNO_3$]

To prepare 1500 ml of solution combine:

1. 68.46 gm crystalline $(NH_4)_2S_2O_8$
2. 300 ml 0.1 N $AgNO_3$ solution

and dilute to 1500 ml using distilled water.

Additional solution should be prepared for at least 1 liter of solution as a blank.

---

*EPA Level I procedure has been changed to use silica gel instead of Drierite.

Impinger #4 (color indicating Drierite)

Use 750 gm or approximately 750 cc of 8 mesh color indicating Drierite ($CaSO_4$)

When installing the top on the impinger bottle, avoid forcing Drierite up into the center tube as this results in increased pressure drop. Lay impinger on side while inserting top.

It may be necessary to replace the Drierite several times during a SASS run. A marked decrease in Impinger #4 outlet temperature (moisture absorption by Drierite produces heat) may signal Drierite depletion if the Drierite color change is difficult to detect.

The spent Drierite is not kept for analysis and can be discarded or, preferably, rejuvenated for future use by heating in a drying oven at 220°F to 250°F to blueness.

A-3.4 Filter Preparation

More than one filter will be required when particulate grain loading is high (i.e., pulverized coal units, cement kilns, etc.). Using stainless steel tweezers, place each filter in a clean, numbered 150 mm glass petri dish. Bake at 220°F for at least three hours in a drying oven, then immediately transfer to a desiccator to cool.

Weigh the petri dish (plus filter). Weigh a second time, preferably several hours later, to confirm the initial weighing. This is the tare weight used to determine the mass particulate catch on the filter.

The type of filter used is a Gelman type A/E binderless glass fiber filter (142 mm diameter), purchased through Scientific Products.

A-3.5 SASS Train Assembly

Transport each separate train component to the sample port area with all sealing caps in place. When removing caps for connection of components, make certain no foreign matter enters the components. If the ambient dust level is high, the train should be covered with plastic drop cloths. Before installing the probe nozzle and with the probe capped, turn on the vacuum pump and leak check the system. Leakage rate should be held to 0.05 cfm at 20 "Hg pump suction. Avoid overtightening fittings and clamps.

A-3.6 SASS Chemical "Blanks"

a. Blanks from impingers #2 and #3 should be prepared in the field with the same distilled water used in preparing the impinger solution. To prepare a 1000 ml blank, mix the following ingredients and dilute to 1000 ml with distilled water:

   1. 45.7 gm crystalline $(NH_4)_2 S_2O_8$

   2. 200 ml 0.1 N A_gNO_3

b. Blanks of impinger #1 can be prepared in the field with the same H_2O_2 and distilled water used for the impinger solution.

c. Blanks of the wash solutions should be obtained in the field (i.e., IPA, 50:50 meth. chlor. - methanol, H_2O).

d. At least one filter blank should be processed in the same manner as sample filters; one blank per test site.

e. At least one blank sample of the XAD-2 resin should be preserved for each test site.

A-4.0 SAMPLING PROCEDURES

The SASS train is basically a high volume Method 5 system modified to collect trace metal and organic compounds which would normally pass through the standard Method 5 train. The major design differences apparent in Figure A-1 are the XAD-2 adsorbent module, multiple cyclone assembly, and new impinger solutions. The SASS train is operated in much the same fashion as a Method 5 train, but there are a number of modifications as discussed below.

A-4.1 Sample Flow and Isokinetic Conditions

To preserve the cyclone "cut-off" points, the sampling flow rate is adjusted to maintain close to 4.0 awcfm (actual wet cubic feet per minute) at the required 400°F cyclone oven temperature conditions. Since isokinetic sampling is also still required, both these constraints are satisfied to as high a degree as possible by selecting the optimum probe nozzle diameter.

After stack velocities, temperatures, and oxygen levels are established by the preliminary stack traverse, the nomogram, Section A-5, may be used to select the proper nozzle diameter and "rough in" the required sampling rate (but see STEP 5 below). However, if stack conditions are encountered that are not covered by the nomogram, the following computational procedure may be used for each sampling location.

EQUATIONS:

$$d = 0.1192 \sqrt{T_s/V_s} \qquad (1)$$

$$Q_{cy} = 281.4\ (V_s)(d^2)/T_s \qquad (2a)$$

$$V_s = [Q_{cy}(T_s)]/[281.4\ (d^2)] \qquad (2b)$$

$$Q_m = Q_{cy}(T_m/860)[1 - (\%H_2O/100)] \qquad (3)$$

d = nozzle diameter (inches)

T_s = stack temperature (°R)

V_s = stack velocity (ft/sec)

Q_{cy} = sample flow rate at cyclones (awcfm)

Q_m = sample flow rate at meter (adcfm)

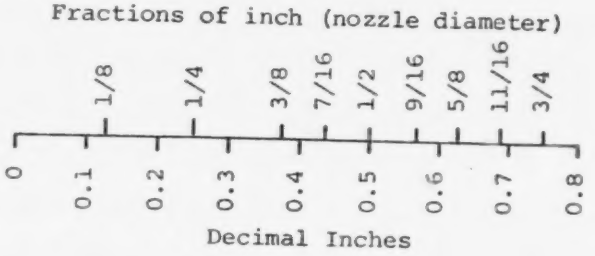
T_m = meter temperature (°R)

$\%H_2O$ = sample moisture content (% by volume)

These equations are valid only when an oven (cyclone) temperature of 400°F is maintained and when the pressure of the stack and dry test meter are roughly the same (i.e., ± 1" Hg).

STEP 1:

Select the nozzle size closest to the value computed from Equation (1). Use this value in the following step:



STEP 2:

Compare the cyclone flow rate from Equation (2a) to the desired rate of 4.0. If the values compare to within ± 10%, proceed to next step. Otherwise, calculate a stack velocity from Equation (2b) using a value for Q_{cy} which is within 10% of 4.0 [i.e., use 3.6 or 4.4, whichever is closest to the value obtained from Equation (2a)]. This calculated stack velocity should be within 10% of the actual stack velocity. If not, stack conditions are very unusual and greater than 10% "tolerances" are necessary (i.e., deviations from isokinetic conditions a/o deviations from 4.0 cfm conditions at the cyclone will be necessary).

STEP 3:

Calculate the meter flow rate from Equation (3) using the cyclone flow determined in the previous step.

STEP 4:

Determine the approximate orifice ΔH corresponding to the flow rate from the previous step. Use the nomogram plot of ΔH versus flow rate determined experimentally for the particular control box and orifice. This is based on the mid-size orifice of the three in the control box.

STEP 5:

The value of ΔH determined in the previous step (or from the nomograph) will be adequate to "rough in" the flow rate when the SASS train is first turned on. However, as soon as possible, obtain more accurate settings using the actual measured meter temperature and the actual meter flow rate obtained from the meter readout and a stopwatch.

A-4.2 Organic Adsorber Module Operation

When the XAD-2 module is operated "cold" to condense moisture from the sample, the following procedure may be used to transfer condensate from the condensate cup at the base of the module to the condensate collection flask. This is necessary to avoid overfilling the condensate cup which would result in condensate carryover into the impingers.

This transfer procedure can be accomplished without interrupting the sampling. The procedure should be performed frequently at the start of a test until the actual condensate collection rate is established.

STEP 1:

Inspect the condensate collection flask and interconnecting tube to confirm that all fittings are tight.

STEP 2:

Partially close off the large (1/2-inch) ball valve at the inlet to the XAD-2 module until the vacuum gage on the pump increases by about 2 in. of mercury.

STEP 3:

Open the condensate drain valve at the bottom of the module. Since the collecting flask is initially at a higher pressure than the inside of the module, air will flow from the flask into the module (bubbling through the collected condensate) until pressures are equalized.

STEP 4:

After a few seconds to allow the equilibration of pressures, open the 1/2-inch ball valve. This raises the pressure in the module relative to the collection flask, forcing any condensate into the bottle.

STEP 5:

After all the condensate has been transferred, close the drain valve.

A-4.3 Drierite

See Section A-2.3 for comments on Drierite depletion and renewal (Impinger #4).

A-4.4 Filter Changes

When sampling combustion effluents with high particulate loading, plugging of the filter may occur before adequate sample volume is obtained. In this event, it will be necessary to shut the train down and install a new filter.

The rate of filter plugging is evident by the gradual increase in sample pump vacuum required to maintain sample flow. To minimize filter changes, the train may be operated with pump vacuums of 15 to 20 "Hg or until desired sample flow cannot be maintained.

A-5.0 TRAIN DISASSEMBLY AND SAMPLE RECOVERY

1. After turning off train and withdrawing probe from stack, open the cyclone oven to expedite cooling (turn oven cooling fan on).

2. Disconnect probe and cap off both probe ends and inlet to 10μ cyclone.

3. Disconnect the line joining the cyclone oven to the XAD-2 module at the exit side of the filter and cap off the filter holder exit and the entrance to the joining line which was disconnected from the filter holder exit point.

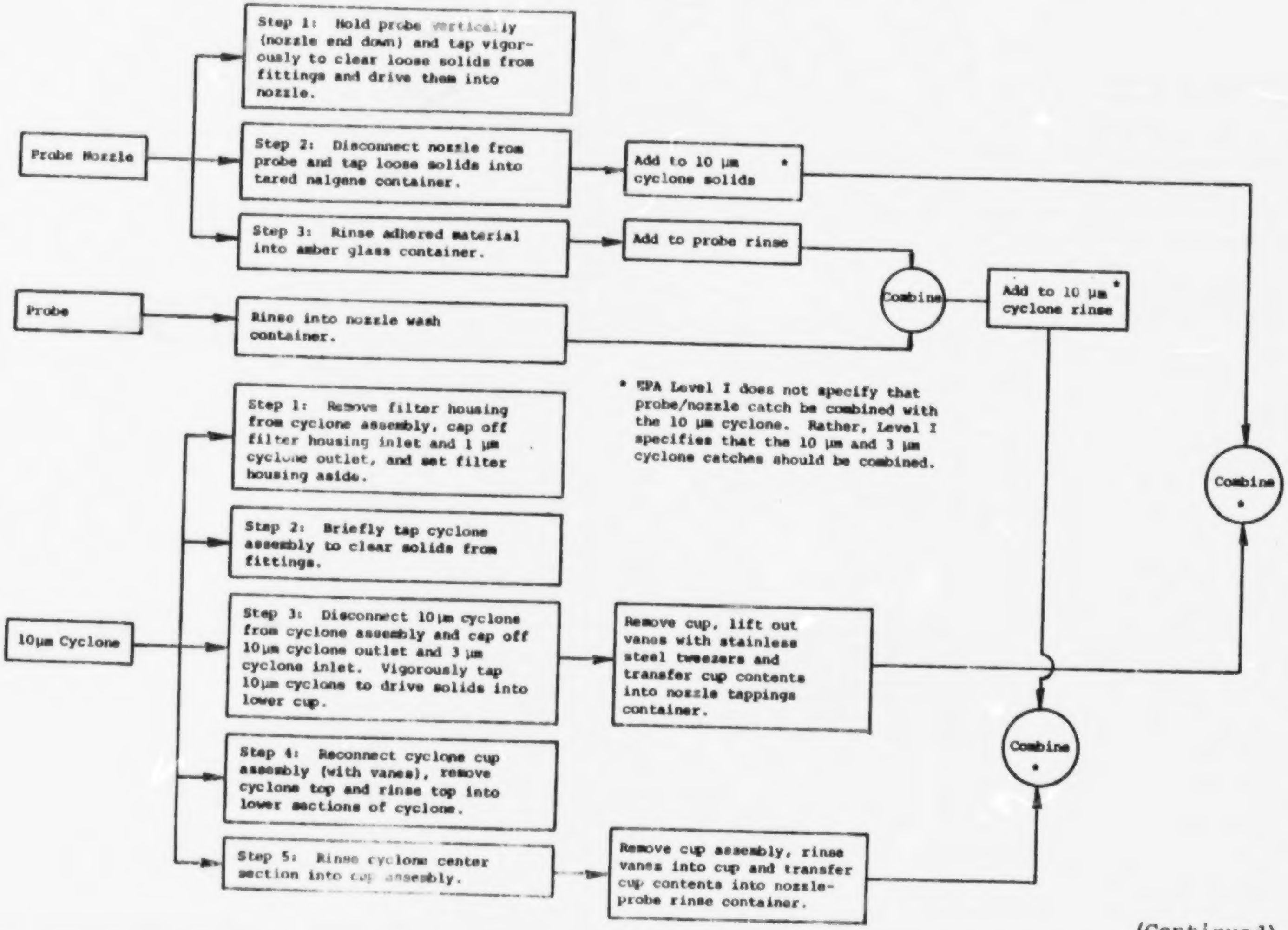
4. Disconnect the line joining the XAD-2 module to the impinger system at the point where it exits the XAD-2 module. Cap off the exit of the XAD-2 module and the entrance to the joining line leading to the impinger system.

5. Disconnect the line exiting the Drierite impinger at the point where it leaves the impinger and cap off the impinger exit. Discard ice and water from the impinger box to facilitate carrying.

6. Carry the probe, cyclone-filter assembly, XAD-2 module (plus joining line and condensate collection flask) and impinger train (plus joining line) to the clean room for sample recovery. Before entering the clean room, clean off all loose particles from the exterior surfaces of the train components using compressed air, brushes, etc.

7. Procedure for transferring samples from the various portions of the SASS train into storage containers is outlined in the flow diagrams on Figures A-2, A-3, and A-4. Place copies of these diagrams in an easily visible location in the clean room for quick reference during the sample recovery and transfer operations.

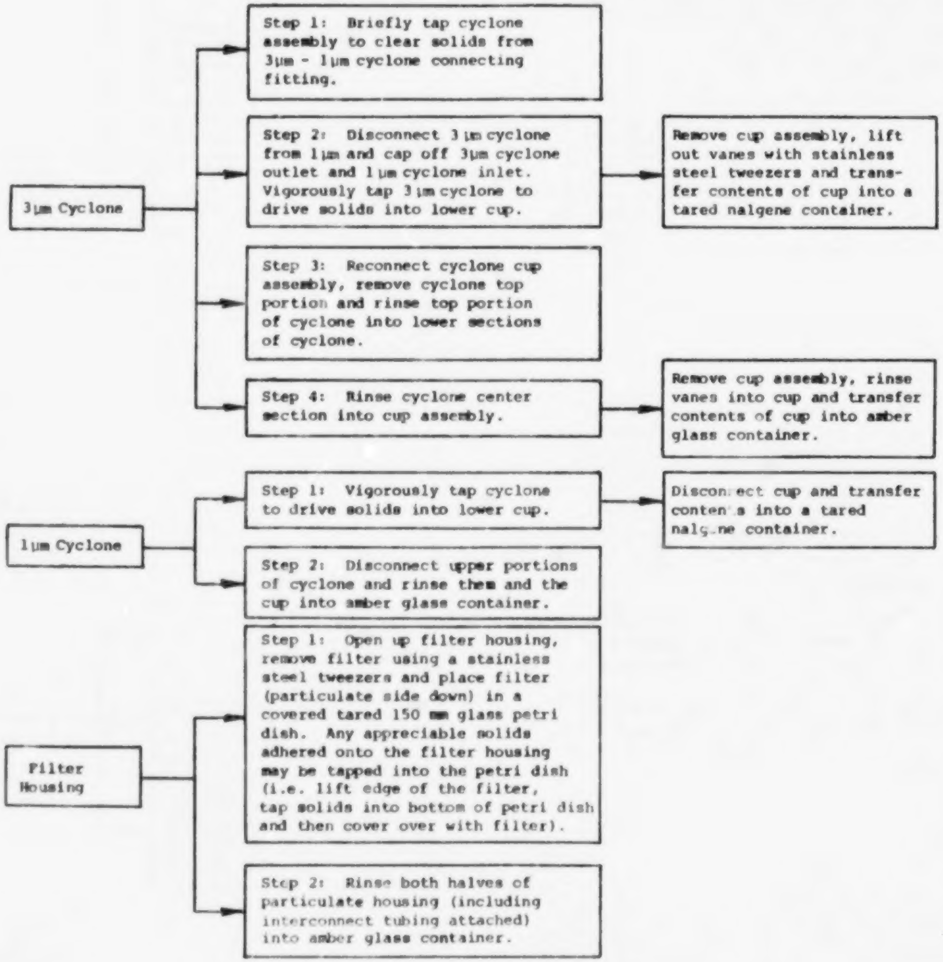
Figure A-2. SASS train sample recovery -- probe, cyclones, filter, XAD-2 module.


Probe Nozzle
Step 1: Hold probe vertically (nozzle end down) and tap vigorously to clear loose solids from fittings and drive them into nozzle.
Step 2: Disconnect nozzle from probe and tap loose solids into tared nalgene container.
Add to 10 µm cyclone solids *
Step 3: Rinse adhered material into amber glass container.
Add to probe rinse
Probe
Rinse into nozzle wash container.
Combine
Add to 10 µm cyclone rinse *
10µm Cyclone
Step 1: Remove filter housing from cyclone assembly, cap off filter housing inlet and 1 µm cyclone outlet, and set filter housing aside.
Step 2: Briefly tap cyclone assembly to clear solids from fittings.
Step 3: Disconnect 10µm cyclone from cyclone assembly and cap off 10µm cyclone outlet and 3 µm cyclone inlet. Vigorously tap 10µm cyclone to drive solids into lower cup.
Remove cup, lift out vanes with stainless steel tweezers and transfer cup contents into nozzle tappings container.
Step 4: Reconnect cyclone cup assembly (with vanes), remove cyclone top and rinse top into lower sections of cyclone.
Step 5: Rinse cyclone center section into cup assembly.
Remove cup assembly, rinse vanes into cup and transfer cup contents into nozzle-probe rinse container.
Combine *
Combine *

* EPA Level I does not specify that probe/nozzle catch be combined with the 10 µm cyclone. Rather, Level I specifies that the 10 µm and 3 µm cyclone catches should be combined.

(Continued)

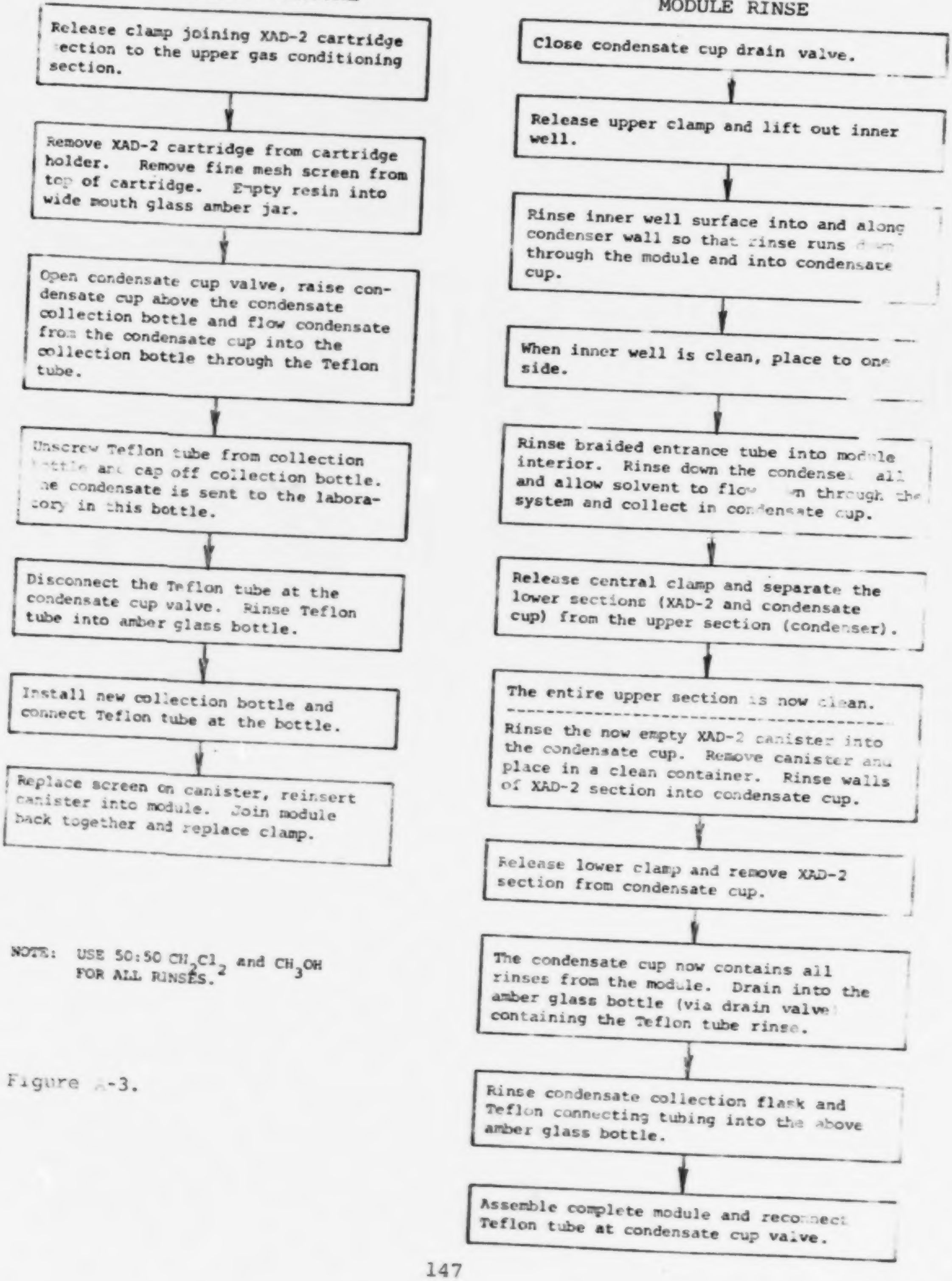
Figure A-2 (continued). SASS train sample recovery -- probe, cyclones, filter, XAD-2 module.


3µm Cyclone
Step 1: Briefly tap cyclone assembly to clear solids from 3µm - 1µm cyclone connecting fitting.
Step 2: Disconnect 3µm cyclone from 1µm and cap off 3µm cyclone outlet and 1µm cyclone inlet. Vigorously tap 3µm cyclone to drive solids into lower cup.
Remove cup assembly, lift out vanes with stainless steel tweezers and transfer contents of cup into a tared nalgene container.
Step 3: Reconnect cyclone cup assembly, remove cyclone top portion and rinse top portion of cyclone into lower sections of cyclone.
Step 4: Rinse cyclone center section into cup assembly.
Remove cup assembly, rinse vanes into cup and transfer contents of cup into amber glass container.
1µm Cyclone
Step 1: Vigorously tap cyclone to drive solids into lower cup.
Disconnect cup and transfer contents into a tared nalgene container.
Step 2: Disconnect upper portions of cyclone and rinse them and the cup into amber glass container.
Filter Housing
Step 1: Open up filter housing, remove filter using a stainless steel tweezers and place filter (particulate side down) in a covered tared 150 mm glass petri dish. Any appreciable solids adhered onto the filter housing may be tapped into the petri dish (i.e. lift edge of the filter, tap solids into bottom of petri dish and then cover over with filter).
Step 2: Rinse both halves of particulate housing (including interconnect tubing attached) into amber glass container.

NOTES:

1. Use 50:50 CH_2Cl_2 and CH_3OH for all rinses (use teflon wash bottles or Guth unitized wash bottles).
2. Handle all tared containers with gloves.
3. Transfer of solids may be assisted by the use of stainless steel spatulas and powder funnels. Nylon bristle brushes may also be used if necessary.
4. All nalgene containers must be high density polyethylene.

SASS TRAIN SAMPLE RECOVERY -- XAD-2 MODULE



STEP NO. 1, XAD-2 AND CONDENSATE REMOVAL

Release clamp joining XAD-2 cartridge section to the upper gas conditioning section.

Remove XAD-2 cartridge from cartridge holder. Remove fine mesh screen from top of cartridge. Empty resin into wide mouth glass amber jar.

Open condensate cup valve, raise condensate cup above the condensate collection bottle and flow condensate from the condensate cup into the collection bottle through the Teflon tube.

Unscrew Teflon tube from collection bottle and cap off collection bottle. The condensate is sent to the laboratory in this bottle.

Disconnect the Teflon tube at the condensate cup valve. Rinse Teflon tube into amber glass bottle.

Install new collection bottle and connect Teflon tube at the bottle.

Replace screen on canister, reinsert canister into module. Join module back together and replace clamp.

STEP NO. 2, XAD-2 MODULE RINSE

Close condensate cup drain valve.

Release upper clamp and lift out inner well.

Rinse inner well surface into and along condenser wall so that rinse runs down through the module and into condensate cup.

When inner well is clean, place to one side.

Rinse braided entrance tube into module interior. Rinse down the condenser wall and allow solvent to flow down through the system and collect in condensate cup.

Release central clamp and separate the lower sections (XAD-2 and condensate cup) from the upper section (condenser).

The entire upper section is now clean.

Rinse the now empty XAD-2 canister into the condensate cup. Remove canister and place in a clean container. Rinse walls of XAD-2 section into condensate cup.

Release lower clamp and remove XAD-2 section from condensate cup.

The condensate cup now contains all rinses from the module. Drain into the amber glass bottle (via drain valve) containing the Teflon tube rinse.

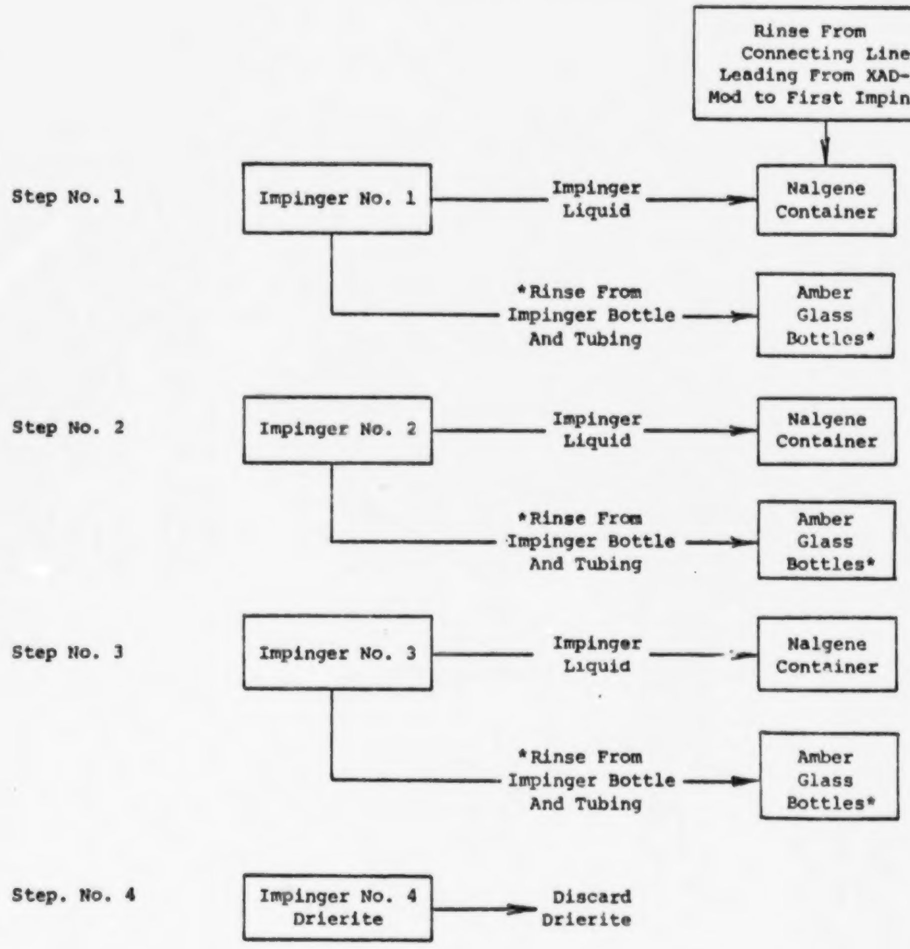
Rinse condensate collection flask and Teflon connecting tubing into the above amber glass bottle.

Assemble complete module and reconnect Teflon tube at condensate cup valve.

NOTE: USE 50:50 CH_2Cl_2 and CH_3OH FOR ALL RINSES.

Figure A-3.

SASS TRAIN SAMPLE RECOVERY -- IMPINGERS



*NOTE: ALL RINSES ARE
(1) ISOPROPYL ALCOHOL (FIRST)
(2) DISTILLED WATER (SECOND)
IPA AND WATER RINSES SHOULD
BE PLACED IN SEPARATE BOTTLES

Figure A-4.

A-6.0 SUPPLEMENTARY REFERENCE MATERIAL

Physical Properties of SASS Chemicals, Figure A-5

Physical Properties of XAD-2, Table A-3

SASS Train Nomogram, Figure A-6

Miscellaneous Data, Table A-4

PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS

No.	Name	Synonyms and Formula	Mol. wt.	Color, crystalline form, specific rotation and λ_{max} (log ε)	m.p. °C	b.p. °C	Density	n_D	Solubility						Ref.
									w	al	eth	ace	bz	other solvents	
	Methane														
Ω m252	—, dichloro-*	Methylene chloride CH_2Cl_2	84.93	λ^{hep} < 200	−95.1	40^{760}	1.3266^{20}_4	1.4242^{20}	δ	∞	∞	...	...	....	$B1^2$, 13
Ω p1588	2-Propanol*	Isopropanol. Isopropyl alcohol. $CH_3CH(OH)CH_3$	60.11	λ^{al} 181 (2.79)	−89.5	82.4^{760}	0.7855^{20}_4	1.3776^{20}	∞	∞	∞	s	v	....	$B1^3$, 1439
Ω m349	Methanol*	Carbinol. Methyl alcohol. Wood alcohol. CH_3OH	32.04	λ^{al} 183.3 (2.18)	−93.9	64.96^{760} 15^{73}	0.7914^{20}_4	1.3288^{20}	∞	∞	∞	∞	v	chl s	$B1^3$, 1147

PHYSICAL CONSTANTS OF INORGANIC COMPOUNDS

No.	Name	Synonyms and Formulae	Mol. wt.	Crystalline form, properties and index of refraction	Density or spec. gravity	Melting point, °C	Boiling point, °C	Solubility, in grams per 100 cc		
								Cold water	Hot water	Other solvents
	Ammonium									
a236	peroxydisulfate	$(NH_4)_2S_2O_8$	228.18	col, monocl, 1.498, 1.502, 1.587	1.982	d 120	....	58.2^0	v s	....
	Hydrogen									
h53	oxide	Water. H_2O	18.0153	col liq or hex cr, liq 1.333, sol 1.309, 1.313	1.000^4_0	0.000	100.000	....	....	∞ al
h64	oxide, per-	H_2O_2	34.01	col liq; 1.414^{22}	1.4422^{25}	−0.41	150.2^{760}	∞	....	s al, eth; i pet eth
n119	Nitric acid	HNO_3	63.01	col liq, corr, pois, $1.397^{16.5}$	1.5027^{25}_4	−42	83	∞	∞	d al, viol, ∞ eth
	Silver									
s167	nitrate	$AgNO_3$	169.87	col, rhomb, 1.729, 1.744, 1.788	4.352^{19}	212	d 444	122^0	952^{100}	s eth, glyc; v sl s abs al

Figure A-5. Physical properties of SASS chemicals.

TABLE A-3. XAD-2 RESIN

XAD-2 is available from:

Fluid Process Department
Rohn and Haas
Philadelphia, Pa.

A contact for questions is:

Mr. Charles Dickert
(215) 592-3000

The material is a styrene/divinylbenzene copolymer and the material is supplies wet with a salt solution.

Some relevant parameters are:

mesh range:	20-50
surface area:	300-350 m^2/g
avg. pore dia.:	90A
specific density:	1.02 g/cc
bulk density:	0.4 g/cc
pore volume:	0.85 cc/g

Costs were $96.50/cu. ft.

Property	*Amberlite XAD-2*
Appearance	Hard, Spherical opaque beads.
Solids	51 to 55
Porosity (ml.pore/ml.bead–dry basis)	0.40 to 0.45
Surface Area ($m.^2/g.$–dry basis)	330
Effective Size (mm.)	0.30 to 0.45
Harmonic Mean Particle Size (mm.)	0.45 to 0.60
Average Pore Diameter (A–dry basis)	90
True Wet Density indistilled water (g./ml.)	1.02
Skeletal Density (g./ml.)	1.07
Bulk Density ($lbs./ft.^3$)	40 to 44
(g./cc.)	0.64 to 0.70

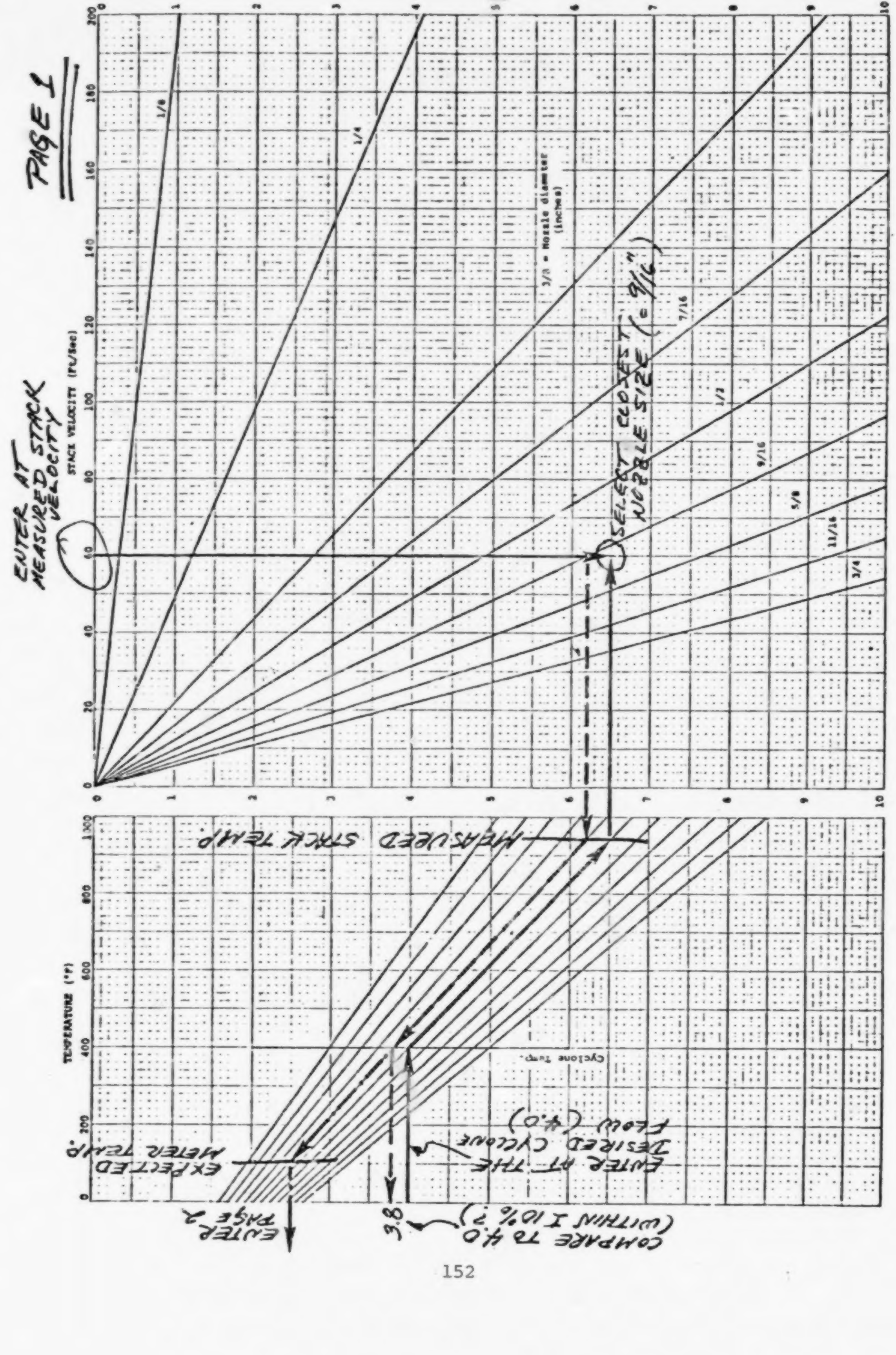
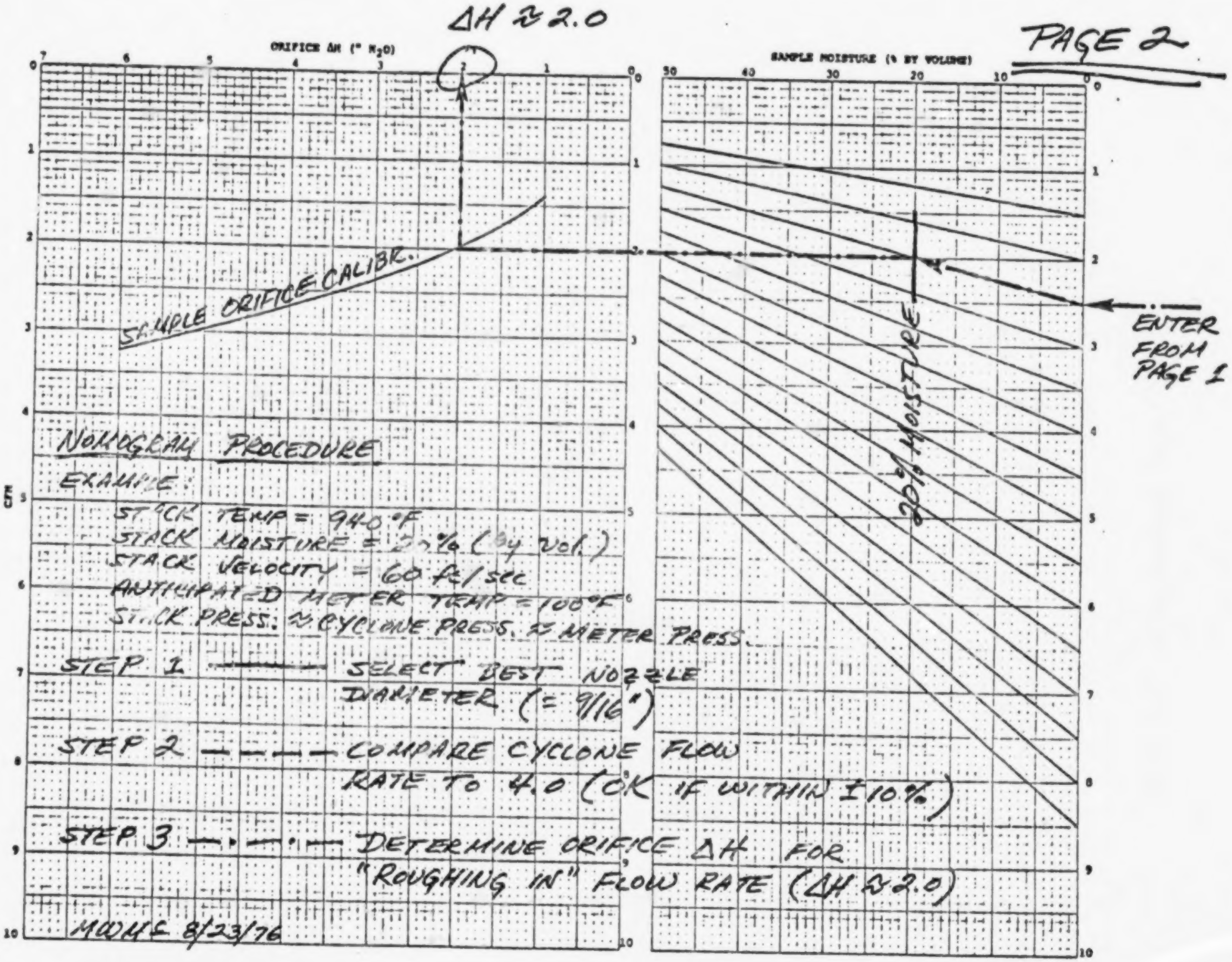


Figure A-6. SASS operating nomogram.



NOMOGRAM PROCEDURE

EXAMPLE:

STACK TEMP = 940 °F
STACK MOISTURE = 20% (By Vol.)
STACK VELOCITY = 60 ft/sec
ANTICIPATED METER TEMP = 100°F
STACK PRESS. ≈ CYCLONE PRESS. ≈ METER PRESS.

STEP 1 ——— SELECT BEST NOZZLE DIAMETER (= 9/16")

STEP 2 – – – – COMPARE CYCLONE FLOW RATE TO 4.0 (OK IF WITHIN ± 10%)

STEP 3 —·—·— DETERMINE ORIFICE ΔH FOR "ROUGHING IN" FLOW RATE (ΔH ≈ 2.0)

MOORE 8/23/76

Figure A-6. (Continued) SASS operating nomogram.

TABLE A-4. MISCELLANEOUS DATA

Cyclone cup capacities: 3 μm and 10 μm = 370 cc; 1 μm = 20 cc

XAD-2 canister volume = 402 cc

S-type pitot tube factor = 0.85 ± 0.2

Screen for XAD-2 canister:
316 stainless steel
80 mesh x 0.055 wire diameter

Purchase from:

Cambridge Wire Cloth Co.
3219 Glendale Blvd
Los Angeles, California
(213) 660-0600

Condensate container volume = 700 cc

XAD-2 module temperature = 68°F (20°C)

A-7.0 SAMPLE PREPARATION AND ANALYSIS (Calspan Corp.)

Samples were analyzed by Calspan Corp., Buffalo, NY, by atomic absorption, gas chromatography and wet chemistry. Spark source mass spectrographic (SSMS) analyses were performed by Commercial Testing and Engineering, Golden, CO, as a subcontract to Calspan's work. Calspan and CTE analyzed preselected samples that include base samples, blanks, and duplicates. Additional samples were submitted to Battelle Memorial Institute, Columbus, OH for analysis of POM by gas chromatograhpy/mass spectrometry.

A-7.1 Sample Size

The sample size required for analysis is dependent on how much sample can be obtained from the SASS train. Table A-5 lists the detection limit and sensitivity for all sample components to be analyzed. For metal analysis, 200 ml of impinger liquids are necessary. For solid samples, 4 to 5 grams are necessary. Analysis for chloride, fluoride, sulfate, and nitrate requires up to 200 ml of liquid sample and 5 grams of solid sample. PCB and POM analysis requires 10 to 50 grams of solids and as much liquid as can be obtained (> 500 ml). Additional sample is required for SSMS analysis.

The sample amounts given are desired amounts. Analysis can be achieved on much smaller samples but with a sacrifice in detection capability for desired components. The detection of individual components, however, cannot be greater than the detection limits and sensitivities given in the table. Detection limits may also be higher for certain types of sample matrix.

A-7.2 Sample Preparation

Analysis of SASS train samples involves pretreatment of the samples after collection to place them in a form suitable for chemical analysis. Atomic absorption requires that each sample be predissolved or be in the liquid phase. The technique for solubilization of the

TABLE A-5. DETECTION LIMITS AND SENSITIVITY VALUES

Pollutant	Detection Limit		Sensitivity	
	Solids (µg/g)*	Liquids (µg/ml)	Solids (µg/g)*	Liquids (µg/ml)
Antimony	10	0.2	25	0.5
Arsenic	0.10	0.002	0.5	0.01
Barium	1.5	0.03	20	0.4
Beryllium	0.25	0.005	1.25	0.025
Cadmium	0.10	0.002	1.25	0.025
Calcium	0.15	0.003	4	0.08
Chromium	1.0	0.02	5	0.1
Cobalt	1.5	0.03	10	0.2
Copper	0.5	0.01	5	0.1
Iron	1.0	0.02	5	0.1
Lead	2.5	0.05	25	0.5
Manganese	0.5	0.01	2.5	0.05
Mercury	0.01	0.0002	0.05	0.001
Nickel	1.0	0.02	7.5	0.15
Selenium	0.1	0.002	0.1	0.002
Tellurium	10	0.2	50	1
Tin	5	0.1	200	4
Titanium	15	0.3	100	2
Vanadium	10	0.2	40	0.8
Zinc	0.25	0.005	1	0.02
Chloride	5.0	1	250	5
Fluoride	5	0.1	12.5	0.25
PCB	0.1	0.002	0.50	0.01
POM	50	0.1	100	2
Sulfates	50	1	250	5
Nitrates	5	0.1	10	0.2

*Values given are for 1 gram of material dissolved in 50 ml of solution.

metals is based on methods utilized by the National Bureau of Standards* (Ref. A-2) for solubilizing both highly organic materials such as coal and inorganic materials such as fly ash prior to sample analysis. The outlined techniques allow for wet chemical ashing of material that prevents loss of volatile elements like mercury, arsenic, and selenium. The methods given use concentrated minerals acids, as well as a strong oxidizing acid, perchloric ($HClO_3$), to decompose organic materials.

One gram of highly organic material (coal, tar residue, fuel oil, etc.) is transferred to a Teflon beaker. The sample is slowly digested for several hours in 25 ml of NHO_3 and cooled. A mixture of 5 ml of HF and 10 ml of $HClO_4$ is added and the digestion is continued at low heat. Extreme care is necessary, for excessive temperatures can cause decomposition and explosion. Digestion is continued until all carbonaceous material has been destroyed. The solution is then transferred to a 50 ml volumetric flask and diluted to a calibrated volume.

Samples not as highly organic (fly ash, bottom ash, cement kiln dust, etc.) are to be accurately weighed to one gram in a Teflon beaker. A mixture of 5 ml of HNO_3 and 5 ml of HF is added. The beaker is covered and the sample digested for one hour. After complete cooling, 10 ml of $HClO_4$ is added and the digestion is continued until all carbonaceous material has been destroyed. The cover is then removed and the sample evaporated to dryness and baked until the solids turn brown around the edges. A mixture of 2 ml of HCl and 35 ml of distilled water is added and the solution heated slightly until all solids dissolve. The solution is then transferred to a 50 ml volumetric flask and diluted to a calibrated volume.

Liquid samples from the SASS train are stabilized with 1 ml of concentrated nitric acid to every 200 ml of impinger liquid. Whenever possible liquids are concentrated by boiling to one-half their received volume to concentrate trace elements.

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*EPA Level I specifies the use of Parr bombing to avoid loss of volatiles.

Both predissolved and concentrated liquids are analyzed using atomic absorption spectroscopy using the most sensitive aspiration techniques available. Analysis for both PCB and POM will involve extraction and concentration prior to analysis. The PCB and POM are coextracted by liquid-liquid or liquid-solid extraction.

Solid samples (∿ 50 grams) are extracted with pentane using a Soxhlet extractor. The extract is concentrated using a Kuderna-Danish evaporator to reduce the extract volume to 10 ml. Aliquots 2 to 5 μl are injected directly into a gas chromatograph for PCB and POM analysis after liquid-solid column separation and clean-up.

Both POM and PCB after extraction with pentane are isolated as a class using adsorption chromatography by a technique called the Rosen separation (Refs. A-3 and A-4). This technique entails adsorption of the total sample on a silica gel column. The initial effluent from the column when washed with pentane will contain an aliphatic hydrocarbon fraction. The aromatic hydrocarbon fraction is eluted with benzene. The benzene fraction which contains all POM and PCB is analyzed using gas chromatography employing FID and EC detectors.

Detection and measurement of POM and PCB are accomplished by using a gas chromatograph employing a flame ionization detector (FID) and an electron capture (EC) detector equipped with Ni-63 source. Confirmation is performed by comparing to POM standards and PCB standards of known concentration and literature relative retention time data.

A-7.3 Analysis Procedures

Analysis for chlorine, fluorine, nitrates, and sulfates all involve wet chemical processing prior to actual measurement. Since all chlorides, nitrates and most sulfates are water soluble, they can be extracted from solid samples using a Soxhlet extractor. The extraction scheme to be used has been effectively used by the Bay Area Air Pollution Control District, San Francisco (Refs. A-5 and A-6).

Fluorides, however, are not sufficiently soluble to allow for effective aqueous extraction. Solid samples are fused with sodium hydroxide to convert all fluorides to soluble sodium fluoride. The fused melt is dissolved in 4 M HCl and the resulting liquid analyzed as a soluble fluoride.

Liquid samples analyzed for chlorine, fluorine, nitrates, and sulfates are analyzed directly by techniques specific for each anion.

Solubilized chloride is analyzed by adding dilute mercuric nitrate solution to an acidified sample in the presence of mixed diphenylcarbozone-bromophenol blue indicator. The end point of the titration is the formation of a blue-violet mercury, diphenylcarbozone complex (Ref. A-7).

An alternative method involves direct measurement of chloride with a specific ion electrode. Both methods are used and checked to obtain the best sensitivity on the submitted samples.

Analysis for fluoride in liquid samples or solubilized fusion products is performed by prior Bellack Distillation to remove interfering substances. After distillation, the fluoride is determined potentiometrically using a selective ion fluoride electrode (Ref. A-8).

The analysis for nitrate is based upon the reaction of the nitrate ion with brucine sulfate in a 13N H_2SO_4 solution at 100°C. The color of the resulting complex is measured at 410 nm (Ref. A-8).

Sulfate analysis is performed by converting sulfate ion to barium sulfate suspension under controlled conditions. The resulting turbidity is determined on a spectrophotometer and compared to a curve prepared from standard sulfate solutions (Ref. A-8).

Metal analyses are performed on liquid and solid samples after pretreatment and solubilization of materials as outlined earlier. A Perkin-Elmer Model 460 atomic absorption spectrometer with microcomputer electronics is used in conjunction with conventional aspiration and time integration techniques. The Model 460 is a relatively new, highly sensitive instrument that allows accurate measurement of metal concentrations. In addition, conventional hollow cathode source lamps, electrodeless discharge lamps (EDL), are available for lead, mercury, arsenic, and selenium. These special lamps are more stable and provide for more initial energy to allow accurate detection of difficult-to-analyze elements.

Mercury is analyzed by the cold vapor technique developed by Hatch and Ott (Ref. A-9). Arsenic and selenium are to be analyzed by conversion of these elements with hydrogen to arsenic hydride and selenium hydride vapor. Each of the vapor techniques allows for low-level detection and quantization for each of these elements.

A listing of the detection limits and sensitivity for each element in liquid and solid samples is given in Table A-6. In the table, detection limit is defined as the concentration that produces a signal equivalent to twice the magnitude of the background. Sensitivity is defined as the concentration in micrograms per milliliter of solution to produce a one percent change in absorption or one percent change in the recording chart readout.

The detection limits for solid samples are based on a one gram sample dissolved or extracted into 50 ml volumes of analysis solution. Each value given is conservative and is based on the possibility of interference between components present. If the sample is relatively "clean", i.e., no interfering or high background substances, detection limits may be even lower.

Polychlorinated biphenyls (PCB) and polycyclic organic materials (POM) are analyzed by Calspan using a Hewlett-Packard Model 5700 gas chromatograph equipped with a flame ionization and an electron capture detector. The electron capture detector contains a radioactive source, Ni-63, and is highly sensitive to chlorinated and highly conjugated organic compounds. The flame ionization detector is sensitive to all hydrocarbons. The gas chromatographic column used in separation of components is four feet long, packed with a substrate coated with 2.5% by weight of a liquid crystal.

The analysis column used is the one suggested by Janini (Ref. A-10) specifically for POM separations. Gas chromatographic column parameters are summarized below:

Column length:	4' x 1/8" OD
Column material:	Stainless steel
Stationary phase:	2.5% BMBT*
Support:	Chromosorb W HP, 100/120 mesh
Flow:	40 ml/min helium
Temperature:	235°C, isothermal

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*N, N-bis [p-methoxybenzylidene]- a, a' - bi-p-toluidine

It should be noted that the gas chromatograph is operated in the isothermal temperature mode. This is necessary due to the extreme temperature sensitivity of the electron capture detector. Any attempt to temperature program would result in a gross baseline drift.

Alternate chromatographic methodology and retention time data has been obtained from an analytical method of Gouw, et al. (Ref. A-11) and Lao, et al. (Ref. A-12). Literature column retention time data is available for all the desired POM listed in the request for proposal with the exception of the dibenzo[c,g]carbazole.

Four of the eight POM are commercially available and are used in fixing retention times and in calibrating the instrument response factors for the various components. The 7,12 dimethylbenz[a]anthracene, benzo[a]pyrene, dibenz[a,b]anthracene, and 3-methylcolanthrene POM are obtained from the Eastman Kodak Company in the pure form. The other POM listed are not available from any commercial source known, so literature relative retention time data of the other POM is utilized to fulfill analyses requirements.

The quantitization of total POM is made by taking the total area of all POM and reporting the response area as if it were 9-methylanthracene ($C_{15}H_{12}$, Mol. Wt. 192.26). If PCB is found to be present, the concentration is subtracted from the total hydrocarbon response area. The standards used in measuring PCB response and retention times are known (Aroclor) standards. The eight individual POM specifically required for identification are analyzed separately, and reported as such. The eight materials are also included in the total POM reported values.

A-7.4 Quality Control

Quality control is maintained by two principal modes. Throughout this study a number of samples are analyzed in duplicate to assure precision of results. More importantly, however, carefully prepared analytical standards and blanks are utilized in preparing suitable calibration curves, thereby assuring accurate measurement of data. To test the accuracy, known additions are made to samples that can be obtained in large enough quantity to test for quantitative recoveries.

A-8.0 SAMPLE PREPARATION AND ANALYSIS (Battelle)

Selected samples provided by Calspan as directed by KVB were analyzed for polycyclic organic materials (POM) and polychlorinated biphenyls (PCB) by Battelle Columbus Laboratories to more positively quantify specific compounds.

A-8.1 Sample Extraction and Concentration

XAD-2 samples are Soxhlet extracted with pentane for 24 hours. Liquid samples, except benzene extracts, are liquid-liquid extracted with methylene chloride and dried over magnesium sulfate. If water is noted in the pentane extract of the XAD-2 sample, that sample is also dried over magnesium sulfate. At this point, samples are split in half for PCB and POM analyses, if both are required. All POM samples are spiked with an internal standard and then concentrated by use of a rotary evaporator and then a Kuderna-Danish concentrator.

A-8.2 Sample Separation

All samples for POM analysis are separated by liquid chromatography on 100-200 mesh Silica gel using a stepwise gradient elution. The POM fractions are eluted with 20 percent methylene chloride in petroleum ether. All other fractions are discarded. The samples are concentrated by a Kuderna-Danish concentrator to a volume of approximately 0.5 ml.

A-8.3 POM Analyses

Analysis for all detectable POM species from anthracene through coronene is carried out by capillary gas chromatography-mass spectroscopy. A 30 m SP-2100 glass capillary column is programmed from 150 °C - 270 °C at 2°C/min and held at 270 °C for the remainder of the run. The carrier gas (helium) flow is 20 cm/sec. All injections are splitless, using the Grob technique. The Finnigan 3200 mass spectrometer is operated in the chemical ionization mode using methane as thereagent gas.

Quantitative GC-MS analysis is accomplished by specific ion monitoring. Total POM and concentrations of the specified POMs are reported. All data is normalized to represent the entire sample. The detection limit is 0.1 nanogram.

Qualitative identification is assured by the elution order and isotope patterns of compounds of interest. Since specific ion monitoring is used, almost any potentially interferring species which may be carried through the LC separation scheme is eliminated duirng mass spectral analysis. Retention times (relative to internal standards) and elution order of isotopes are determined by comparison with POM standards.

A-8.4 PCB Analysis

Extracts are placed on previously standardized Florisil to separate the PCBs from possible contaminates. GC analysis is carried out using a 6 ft x 4 mm ID column packed with 11 percent OV-17 plus QF-1 and an electron capture detector. Sample peaks at retention times relative to aldrin are observed for possible interference. Samples are quantitated against Arochlor 1248. The limit of detection is 150 (total) nanograms. The clean-up procedure using Florisil assures removal of almost all interferring chlorinated pesticides.

REFERENCES FOR APPENDIX A

A-1 Hamersma, J. W., Reynolds, S. L., and Maddalone, R. F., "IERL-RTP Procedures Manual: Level I Environmental Assessment," EPA Report EPA-600/2-76-160a, NTIS Order No. PB 257 850, June 1976.

A-2 Private communication with Theodore C. Rains, U. S. Dept. of Commerce, National Bureau of Standards, Washington, DC (1974).

A-3 Rosen, A. A., and Middleton, F. M., *Anal. Chem. 27*, 790 (1955).

A-4 Moore, G. E., Thomas, R. S., and Monkman, J. L., *J. Chromatogr. 26*, 456 (1967).

A-5 Levaygi, D. A., et al., *J. Air Pollution Association 26* (6), 554 (1976).

A-6 Sandberg, J. S., et al., *J. Air Pollution Association 26* (6), 559 (1976).

A-7 ASTM Standards, Part 23, Water & Atmospheric Analysis, p. 273, Method 512-67, Referee Method A (1973).

A-8 Methods of Chemical Analysis of Waters and Wastes, US EPA, EPA-625/6-74-003 (1974).

A-9 Hatch, W. R., and Ott, W. L., "Determination of Sub-Microgram Quantities of Mercury in Solution by a Flameless Atomic Absorption Technique," *Atomic Absorption Newsletter 6*, 101 (1967).

A-10 Janini, G. M., Hohnston, R., and Zrelinski, W., *Anal. Chem. 47*, (1975).

A-11 Gouw, T. H., Whittemore, I. M., and Jentoft, R. E., "Capillary Column Separation of Various Poly Cyclic Aromatic Materials," *Anal. Chem. 42*, 1394 (1970).

A-12 Lao, R. C., Thomas, H., Oja, H., and Dubois, L., "Application of Gas Chromatograph-Mass Spectrometer Data Processor Combination to the Analysis of the Polycyclic Hydrocarbon Content of Airborne Pollutants," *Anal. Chem. 45*, 908 (1973).

APPENDIX B - CONVERSION FACTORS

SI Units to Metric or English Units

To Obtain	From	Multiply By
g/Mcal	ng/J	0.004186
10^6 Btu	GJ	0.948
MBH/ft^2	GJ·hr^{-1}·m^{-2}	0.08806
MBH/ft^3	GJ·hr^{-1}·m^{-3}	0.02684
Btu	gm cal	3.9685×10^{-3}
10^3 lb/hr* or MBH	GJ/hr	0.948
lb/MBtu	ng/J	0.00233
ft	m	3.281
in	cm	0.3937
ft^2	m^2	10.764
ft^3	m^3	35.314
lb	Kg	2.205
Fahrenheit	Celsius	$t_F = 9/5(t_C)+32$
	Kelvin	$t_F = 1.8K - 460$
psig	Pa	$P_{psig} = (P_{pa})(1.450X10^{-4})-14.7$
psia	Pa	$P_{psia} = (P_{pa})(1.450X10^{-4})$
iwg (39.2°F)	Pa	$P_{iwg} = (P_{pa})(4.014X10^{-3})$
10^6 Btu/hr	MW	3.413
GJ/hr	MW	3.60

To Obtain ppm at 3% O_2 of	Multiply Concentration in ng/J by
Natural Gas Fuel	
CO	3.23
HC	5.65
NO or NOx	1.96
SO_2 or SOx	1.41
Oil Fuel	
CO	2.93
HC	5.13
NO or NOx	1.78
SO_2 or SOx	1.28
Coal Fuel	
CO	2.69
HC	4.69
NO or NOx	1.64
SO_2 or SOx	1.18

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*lb/hr of equivalent saturated steam

English and Metric Units to SI Units

To Obtain	From	Multiply By
ng/J	lb/MBtu	430
ng/J	g/Mcal	239
$GJ \cdot hr^{-1} \cdot m^{-2}$	MBH/ft^2	11.356
$GJ \cdot hr^{-1} \cdot m^{-3}$	MBH/ft^3	37.257
GJ/hr	10^3 lb/hr* or 10^6 Btu/hr	1.055
m	ft	0.3048
cm	in	2.54
m^2	ft^2	0.0929
m^3	ft^3	0.02832
Kg	lb	0.4536
Celsius	Fahrenheit	$t_C = 5/9\ (t_F-32)$
Kelvin		$t_K = 5/9\ (t_F-32) + 273$
Pa	psig	$P_{pa} = (P_{psig} + 14.7)(6.895X10^3)$
Pa	psia	$P_{pa} = (P_{psia})(6.895X10^3)$
Pa	iwg (39.2°F)	$P_{pa} = (P_{iwg})(249.1)$
MW	10^6 Btu/hr	0.293
MW	GJ/hr	0.278

To Obtain ng/J of	Multiply Concentration in ppm at $3\%\ O_2$ by
Natural Gas Fuel	
CO	0.310
HC	0.177
NO or NOx (as equivalent NO_2)	0.510
SO_2 or SOx	0.709
Oil Fuel	
CO	0.341
HC	0.195
NO or NOx (as equivalent NO_2)	0.561
SO_2 or SOx	0.780
Coal Fuel	
CO	0.372
HC	0.213
NO or NOx (as equivalent NO_2)	0.611
SO_2 or SOx	0.850

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*lb/hr of equivalent saturated steam